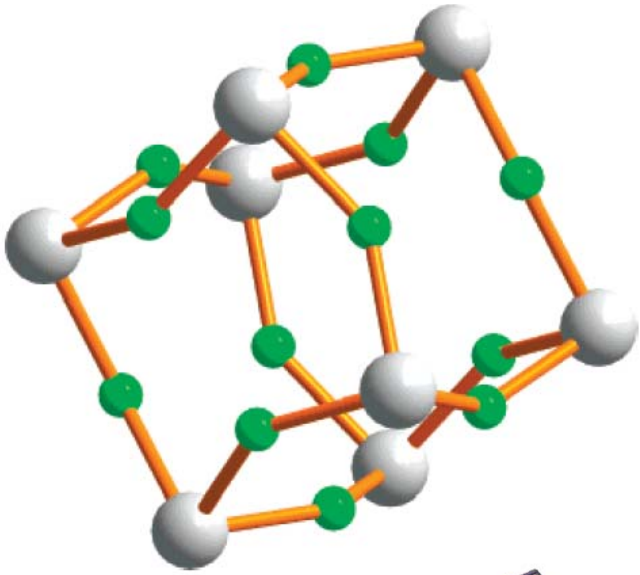
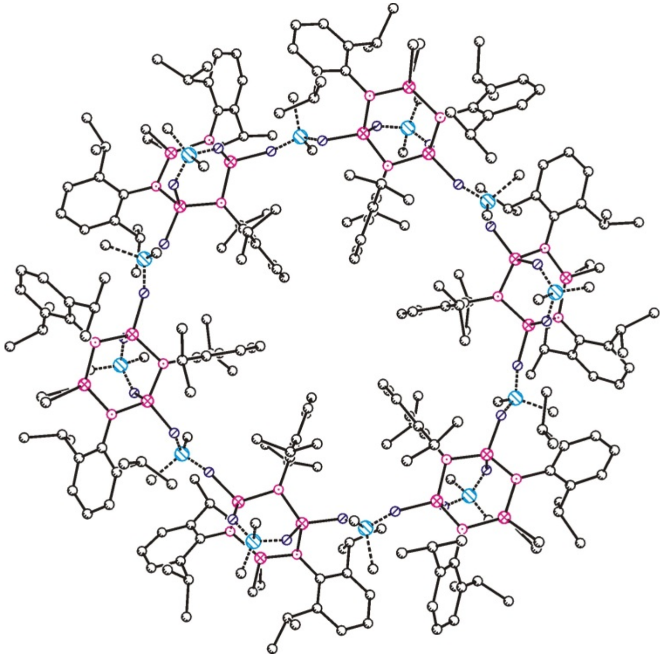
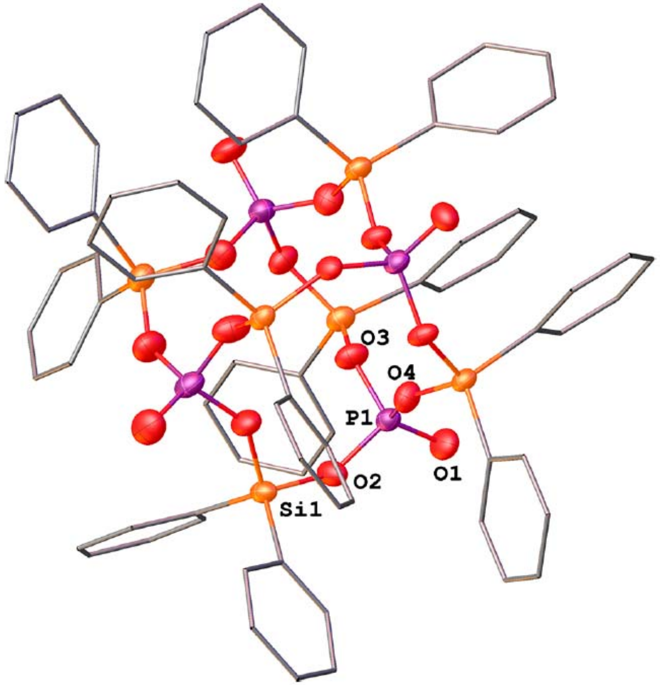
Rings and Polyhedra



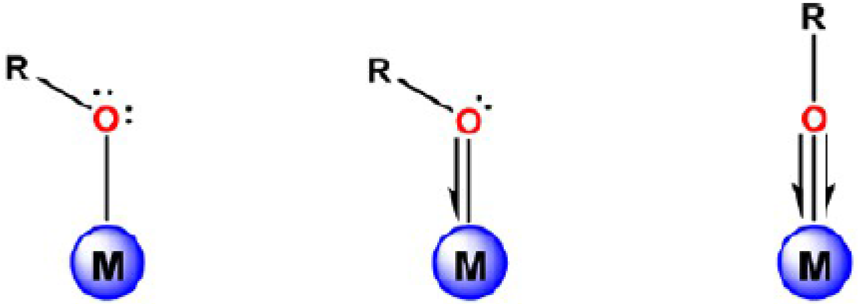




Coordination Modes

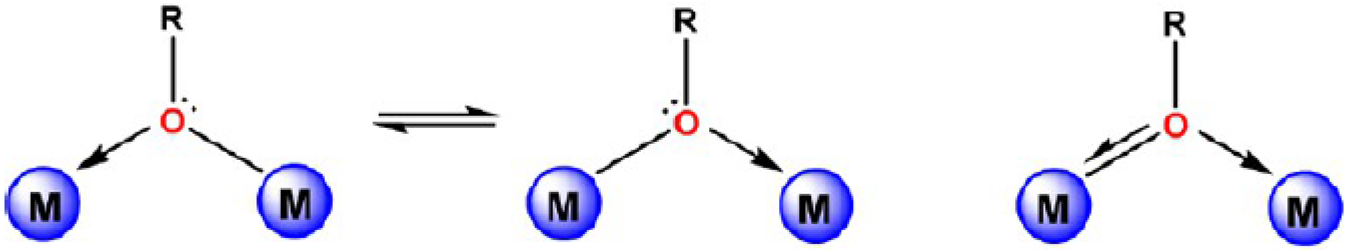
alkoxide

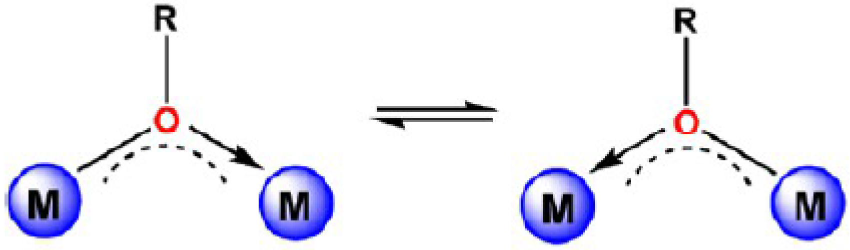
terminal



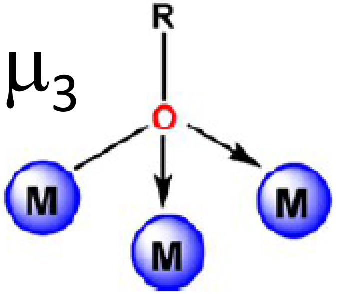
bridging

μ_2





μ_3



“Harris” Notation

J. Chem. Soc., Dalton Trans., 2000, 2349

The binding mode is referred to as $[X.Y_1Y_2Y_3\ .\ .\ .Y_n]$

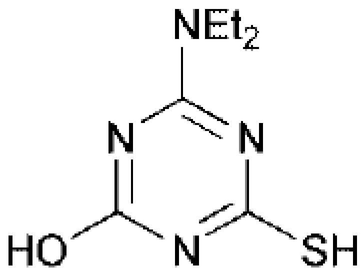
X = the **overall** number of **metals** bound by the whole ligand

Each value of Y refers to the **number** of metal atoms **attached** to the different donor atoms

n = number of donor atoms
The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules

The ligand $OStaH^-$ has three donor atoms
S, O and N(1)
So the notation includes three values of Y
Ordered : **S > O > N**

H_2OSta



“Harris” Notation

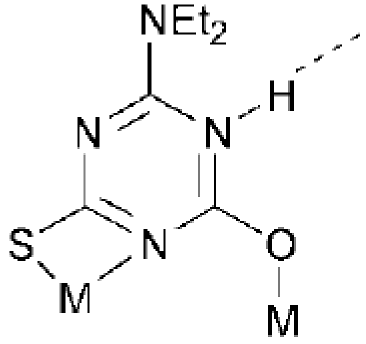
S > O > N

If the ligand is bound to more than one metal, and is chelating, it is difficult to indicate whether the N-donor is bound to the same metal as the sulfur or oxygen atom.

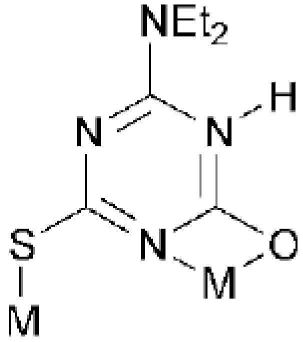
While the chelating N,S mode is inherently more likely (and observed), there is still a need to distinguish between this and the N,O-chelating mode.
To distinguish between these two alternatives include a **subscript** number to show to which **metal atom** the donor is attached.

The mode [$2.1_{\mathbf{1}}1_{\mathbf{2}}1_{\mathbf{1}}$] implies the N- and S-donors chelate to one metal and the O atom binds to the second metal

The mode [$2.1_{\mathbf{1}}1_{\mathbf{2}}1_{\mathbf{2}}$] implies the N- and O-donors chelate and the S-donor binds to the second metal



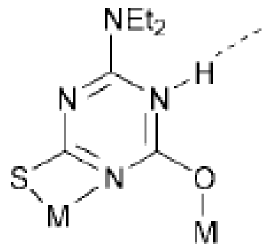
$2.1_1 1_2 1_1$



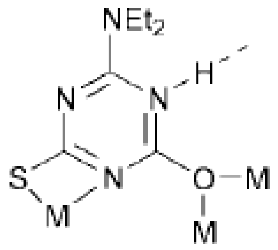
$2.1_1 1_2 1_2$

“Harris” Notation

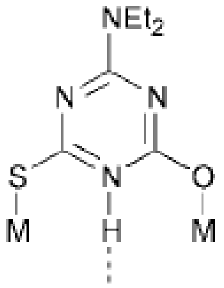
S > O > N



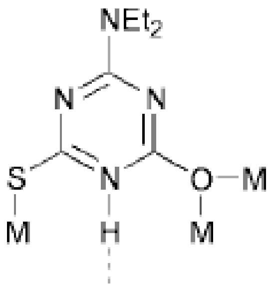
$2.1_1 1_2 1_1$



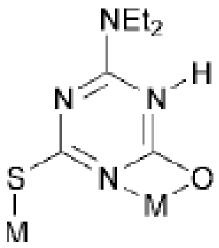
$3.1_1 2_{23} 1_1$



2.110



3.120



$2.1_1 1_2 1_2$

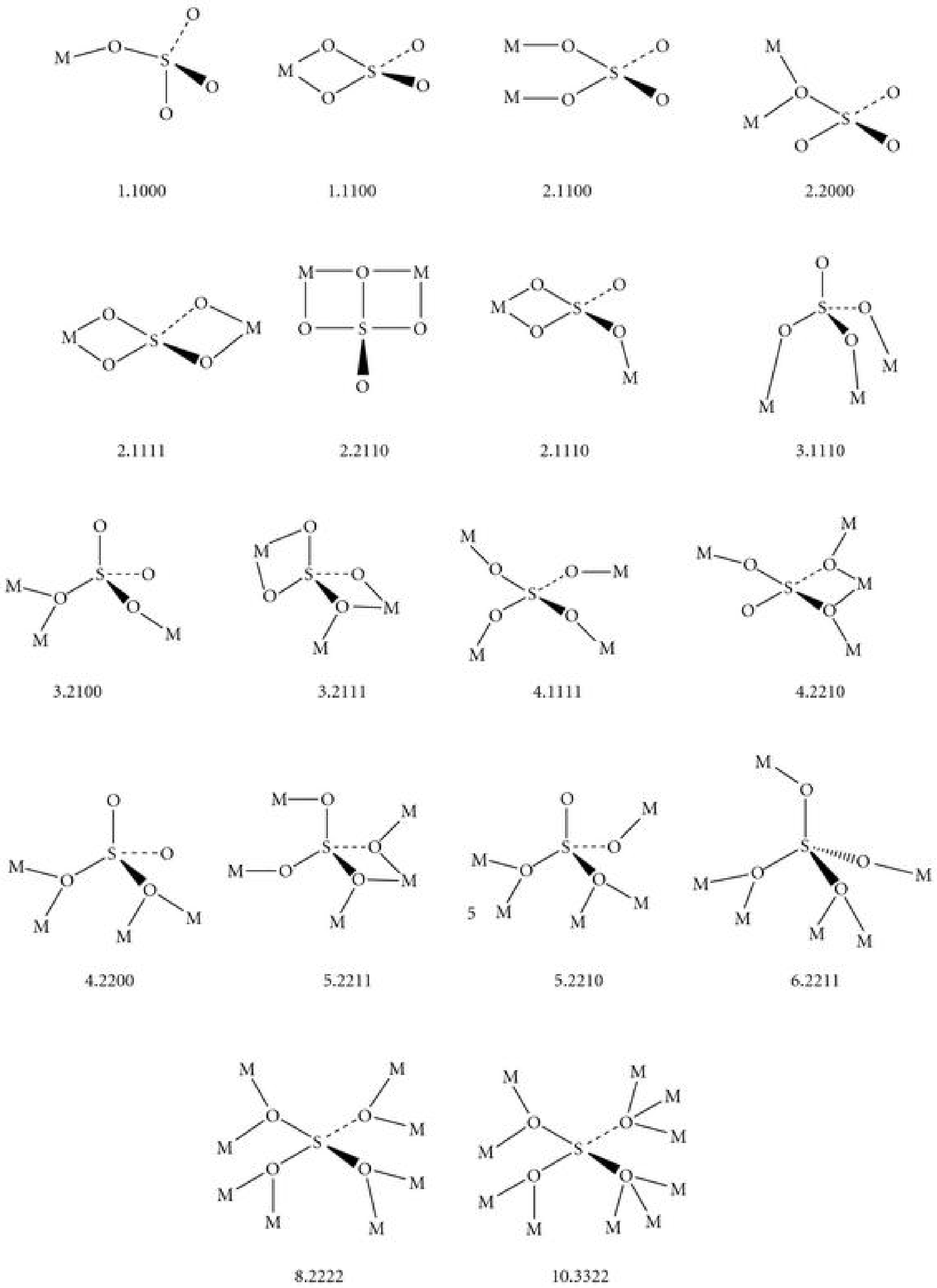
Five possible bonding modes for ligand OStaH^{-}

The numbers below each bonding mode refer to the Harris notation

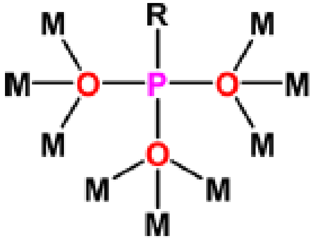
The mode [$2.1_{\mathbf{1}}1_{\mathbf{2}}1_{\mathbf{2}}$] shows how Harris notation distinguishes between possible binding modes (*cf.* [$2.1_{\mathbf{1}}1_{\mathbf{2}}1_{\mathbf{1}}$]).

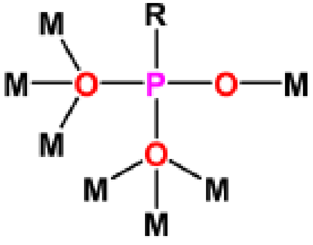
The dashed lines to H atoms indicate hydrogen bonds

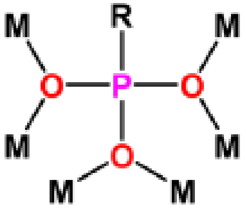
Crystallographically established coordination modes of the sulfato ligand

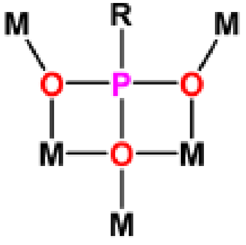


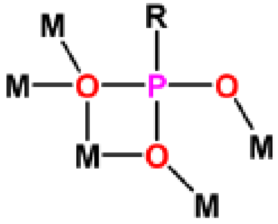
Coordination modes of the phosphonato ligand

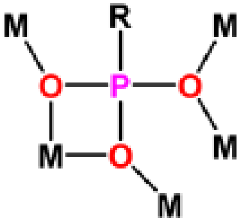

9.333


7.331


6.222


5.232


5.321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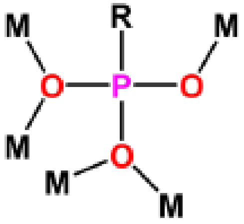
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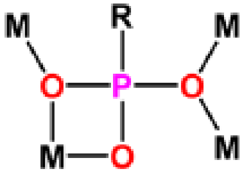
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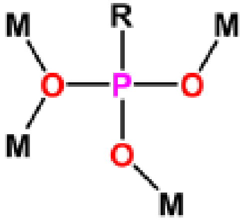
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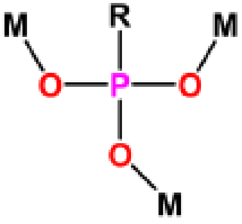
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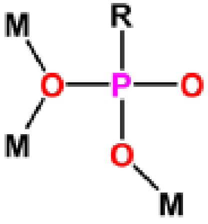
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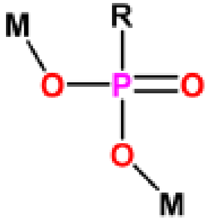
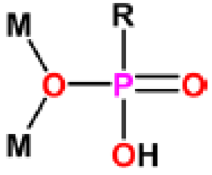
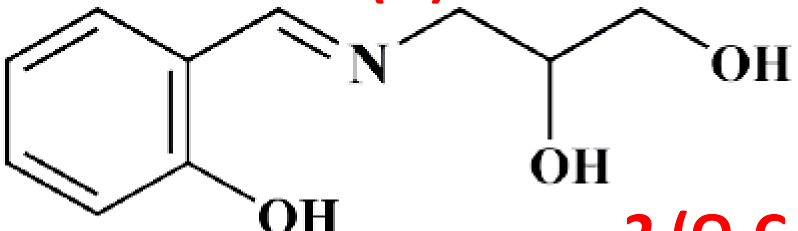

2.110


2.200

“Harris” Notation

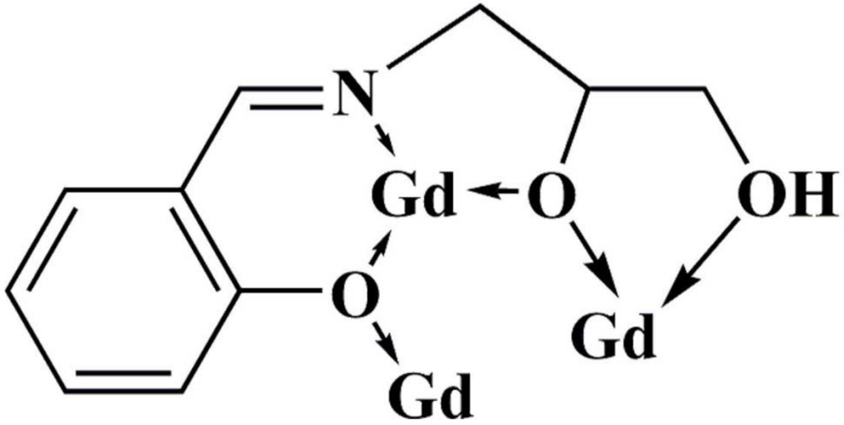


4 (N)

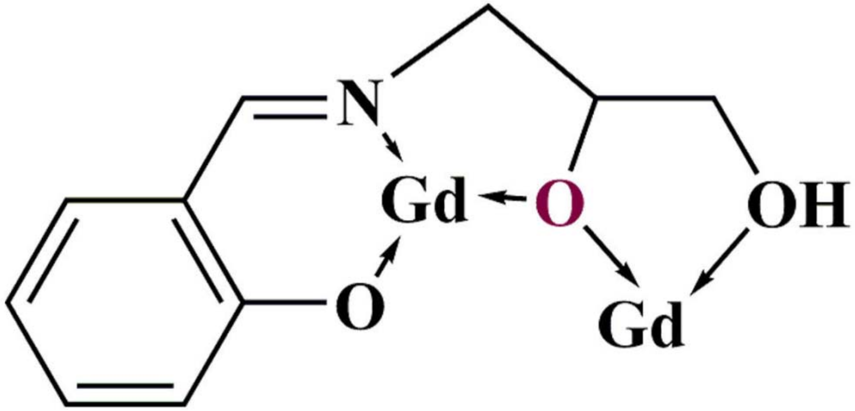
3 (O-C-CH2)

2 (O-C-C2H)

1 (O-C-C3)



3.2211



2.1211

Symmetry Labels $\mathbf{nx_{yz}}$

Characters in group tables
the labels can be used to describe the symmetry of orbitals

n = orbitals of the same symmetry are numbered successively in order of increasing energy

x = a - singly degenerate and symmetrical to C_{2n} rotation about the principle rotation axis
x = b - singly degenerate and unsymmetrical to C_{2n} rotation about the principle rotation axis
x = e - doubly degenerate
x = t - triply degenerate

y = 1 - symmetrical to reflection through a reference mirror plane
y = 2 - unsymmetrical to reflection through a reference mirror plane

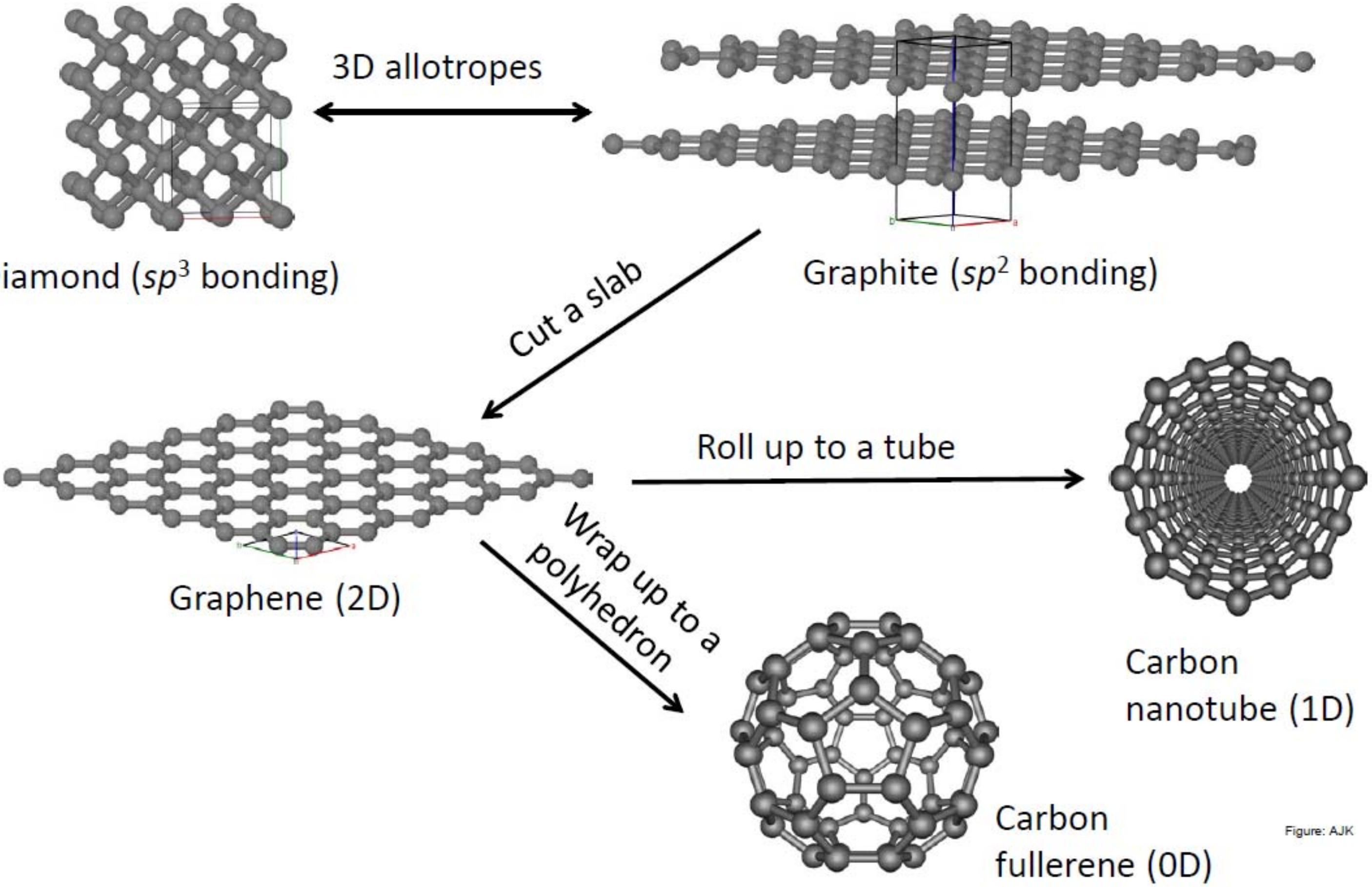
z = 'nothing' if there is no inversion center
z = g - symmetrical to inversion
z = u - unsymmetrical to inversion

e_g

t_{2g}

$1a_{1g}$

Allotropes of Carbon



3D allotropes

Diamond (sp^3 bonding)

Graphite (sp^2 bonding)

Cut a slab

Graphene (2D)

Roll up to a tube

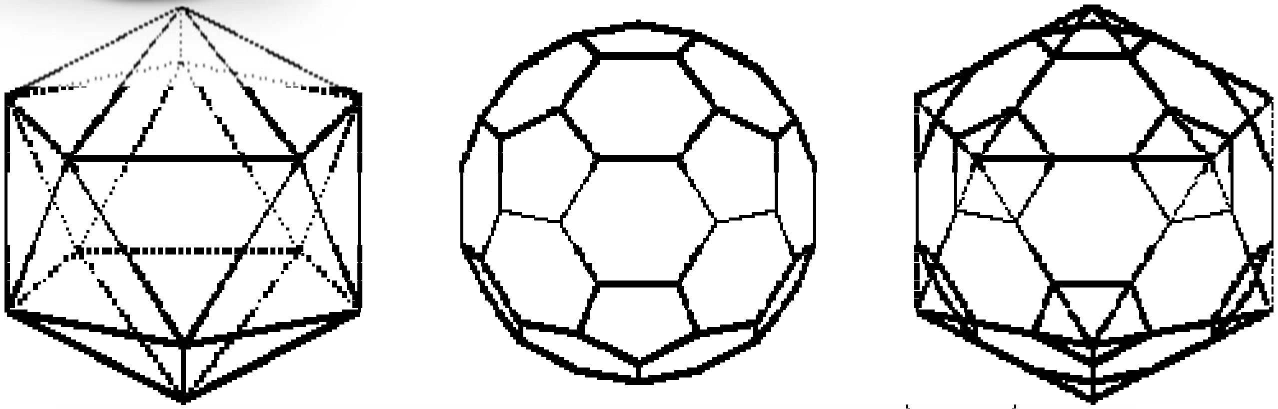
Carbon nanotube (1D)

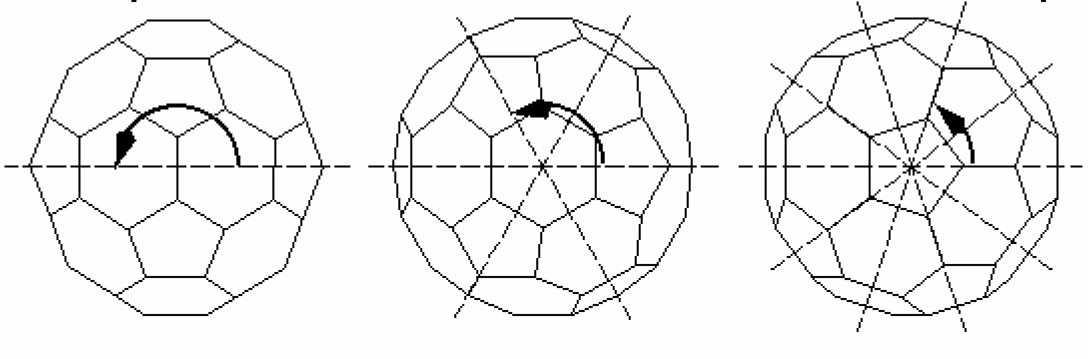
Wrap up to a polyhedron

Carbon fullerene (0D)

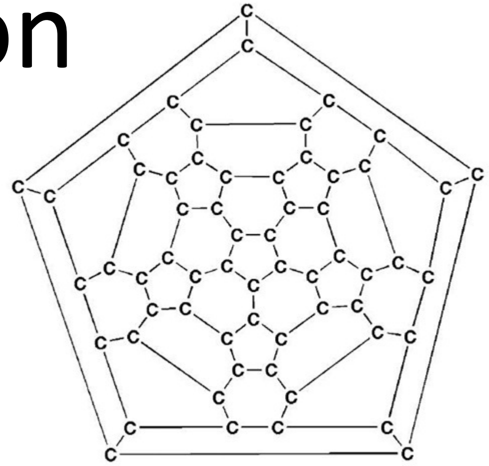
Figure: AJK

Allotropes of Carbon

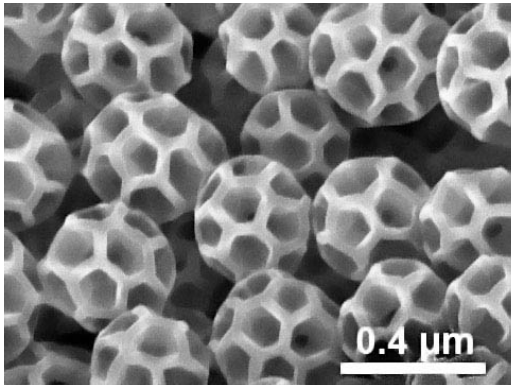




2-fold 3-fold 5-fold



Schlegel diagram

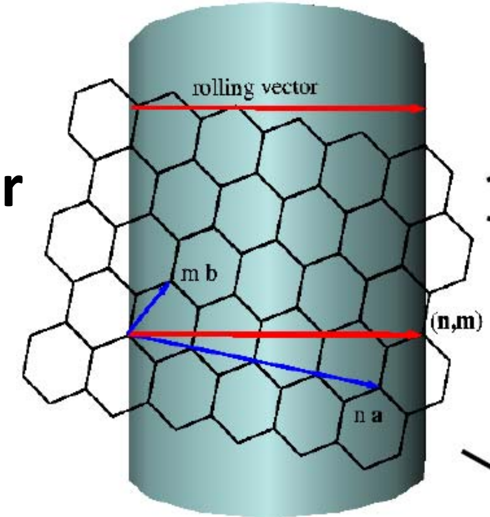


brochosomes

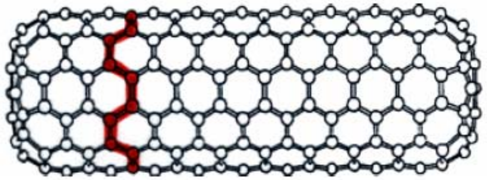
12 pentagonal faces - 6 pairs of opposite faces with a 5-fold rotation axis
20 hexagonal faces - 10 pairs of opposite faces with a 3-fold rotation axis
60 pentagonal edges surrounding the pentagonal faces
30 hexagonal edges lying between two hexagons with a 2-fold rotation axis

(n,m) SWNTs

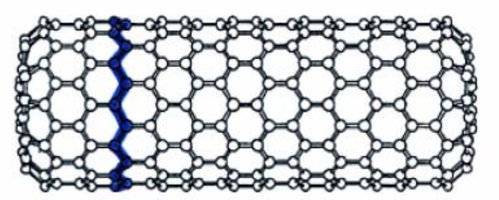
Chiral vector (n,m)



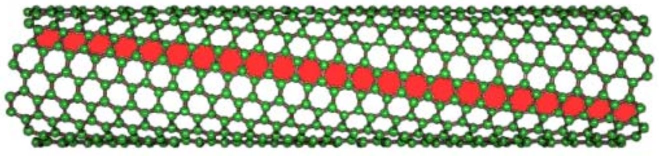
(n,n)
armchair

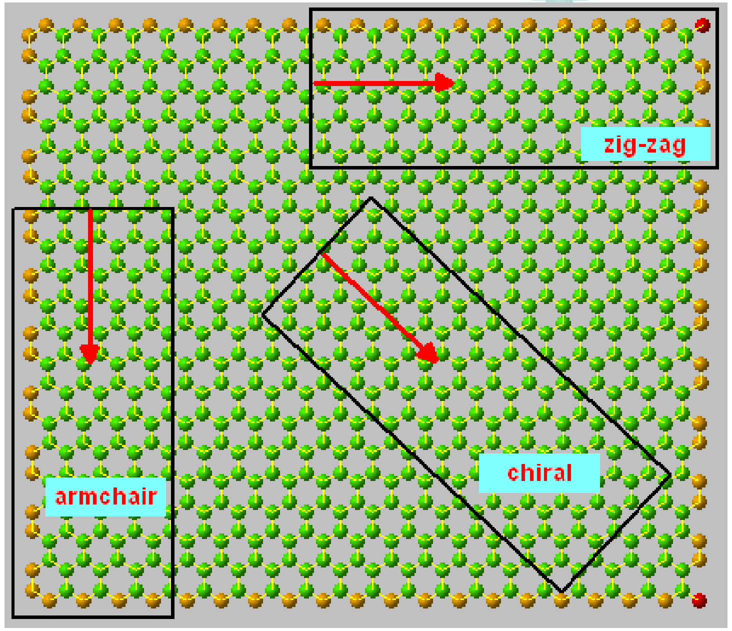


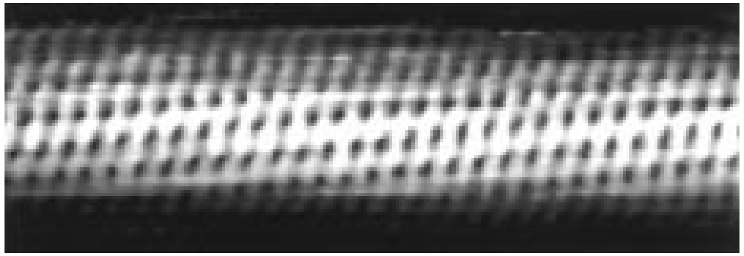
(n,0)
zigzag



(n,m)
chiral

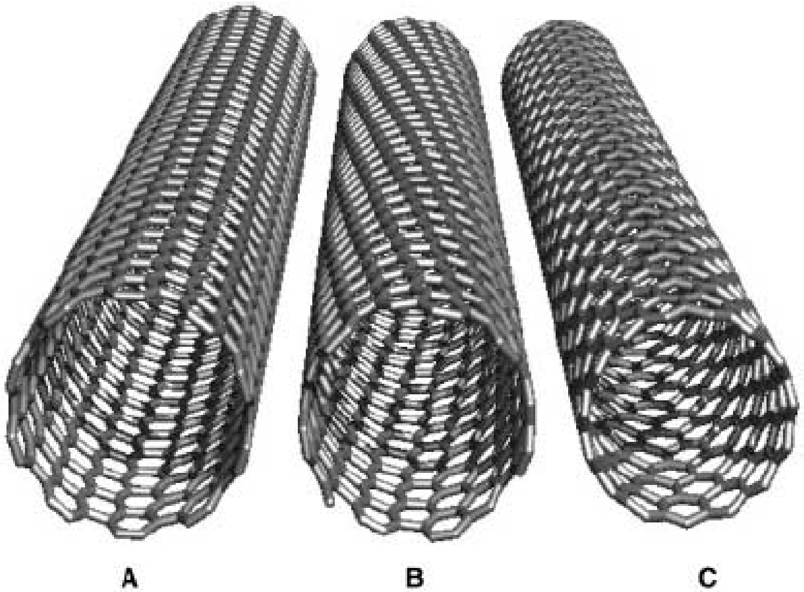


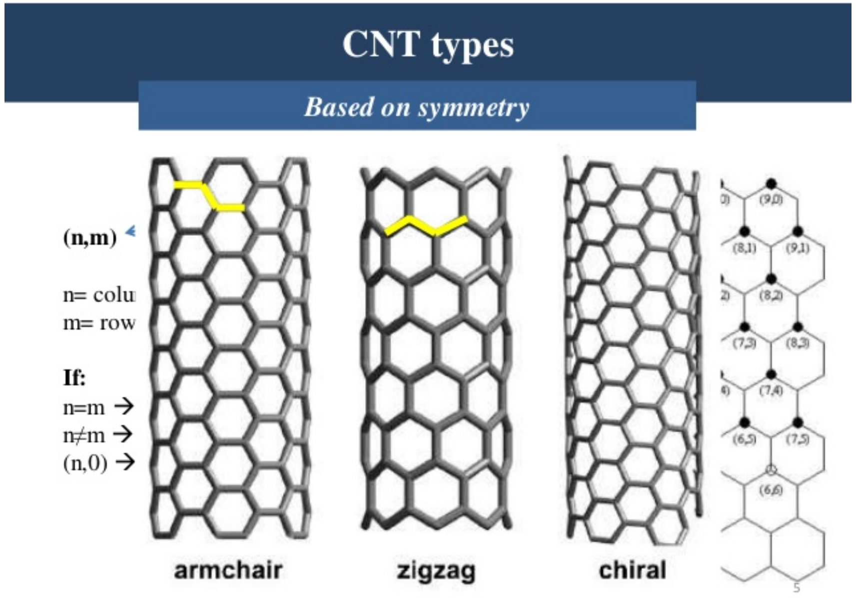




TEM of a chiral CNT

(n,m) SWNTs

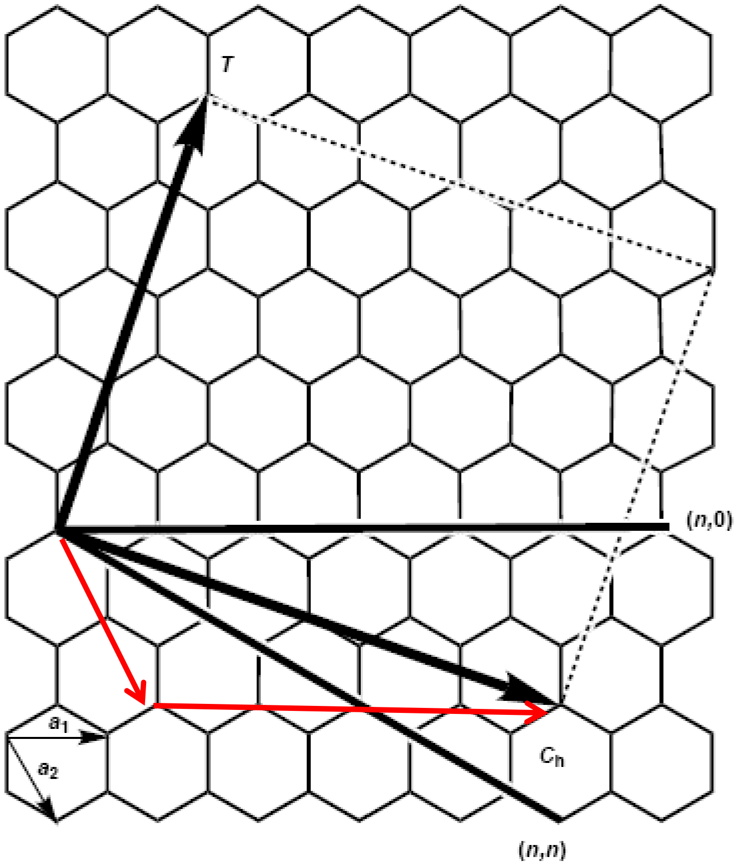




A) Armchair - an achiral metallic conducting (10,10) tube
B) Chiral - semiconducting (12,7) tube
C) Zigzag - an achiral conducting (15,0) tube

All the (n,n) armchair tubes are metallic
Chiral or zigzag tubes are metallic only if (n-m)/3 is a whole number, otherwise, they are semiconductors

Roll-up of (n,m) SWNTs



(n,m) = (4,2)

A 2D graphite layer
the lattice vectors a_1 and a_2
Angle of 60°

The roll-up vector $C_h = na_1 + ma_2$

Achiral tubes exhibit roll-up vectors derived from (n,0) (zigzag) or (n,n) (armchair).

The translation vector T is parallel to the tube axis and defines the 1D unit cell.

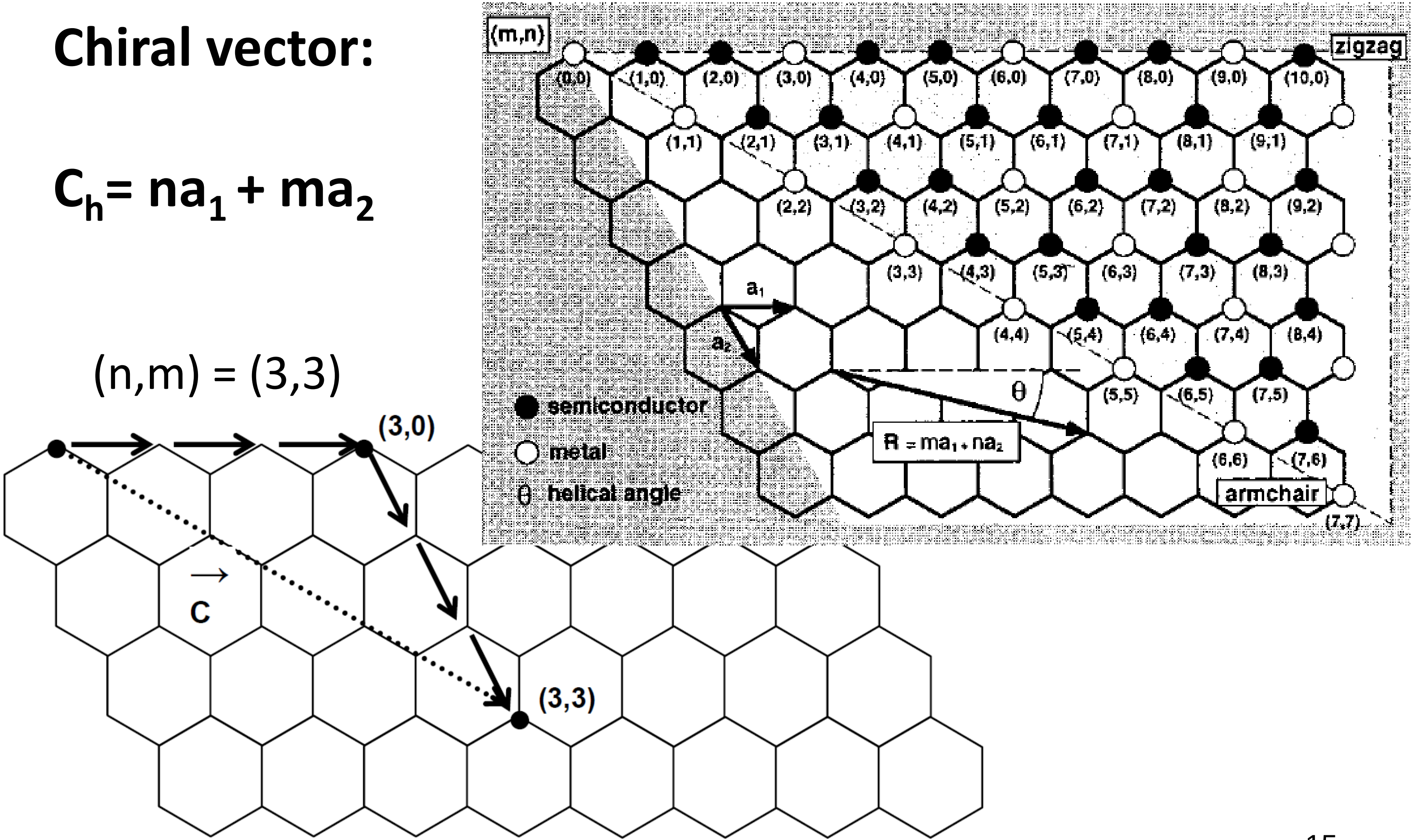
The rectangle represents an unrolled unit cell, defined by T and C_h

Roll-up of (n,m) SWNTs

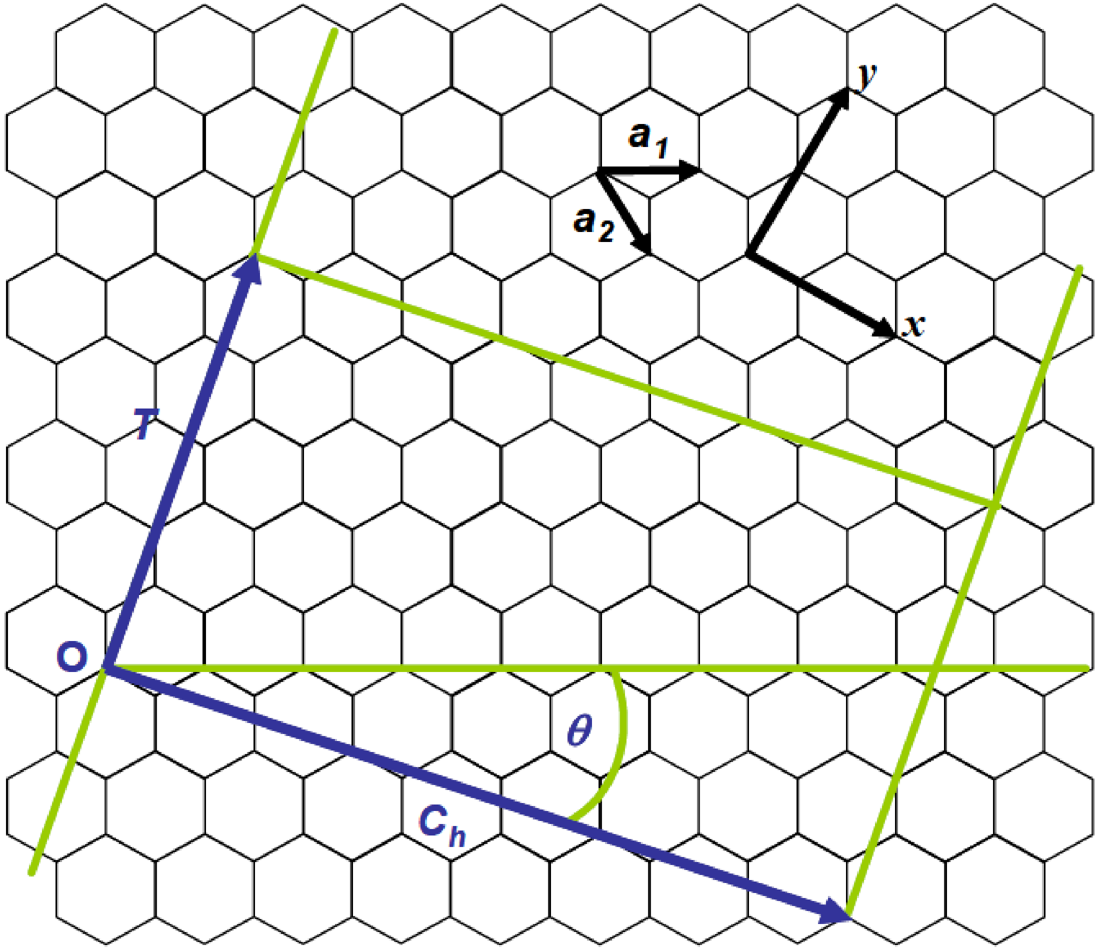
Chiral vector:

$\mathbf{C_h = na_1 + ma_2}$

(n,m) = (3,3)



Roll-up of (n,m) SWNTs



d(Csp^2-Csp^2) = 1.42 Ǻ

$a_0 = a_1 = a_2$

a_0 = 2 d cos(30) =
= 1.42 √3 = 2.49 Ǻ

Roll-up of (n,m) SWNTs

$$\overrightarrow{C_h} = n\overrightarrow{a_1} + m\overrightarrow{a_2} \equiv (n,m) \qquad (\text{ and } \; 0 \le |m| \le n \;)$$

Tube diameter

$$d_t = \frac{|C_h|}{\pi} = \frac{a_0\sqrt{\left(n^2 + nm + m^2\right)}}{\pi}$$

$$|a_1| = |a_2| = a_0 = 0.249 \text{ nm}$$

$$\theta = \tan^{-1}\left[\sqrt{3}m/(m+2n)\right]$$

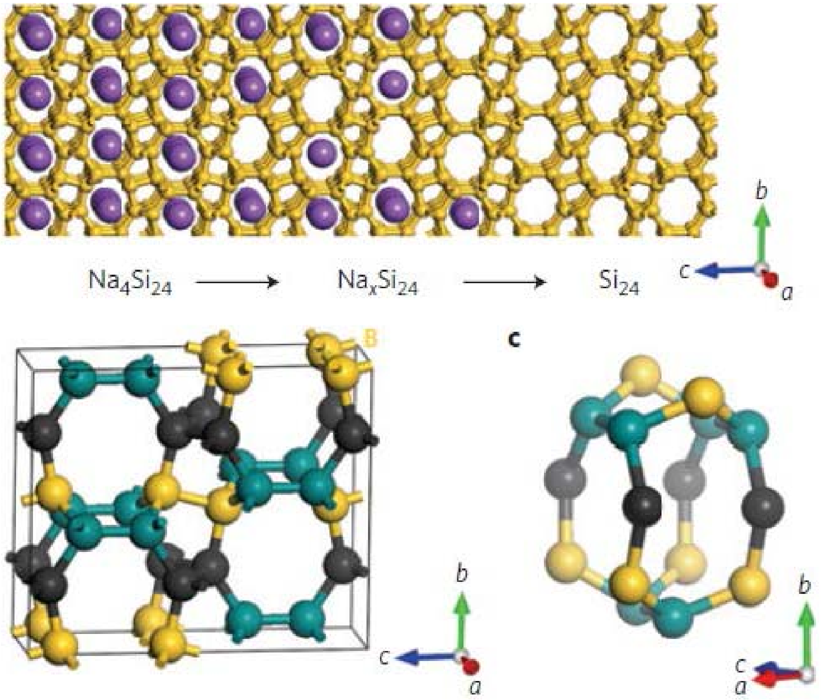
θ = 0 - 30°

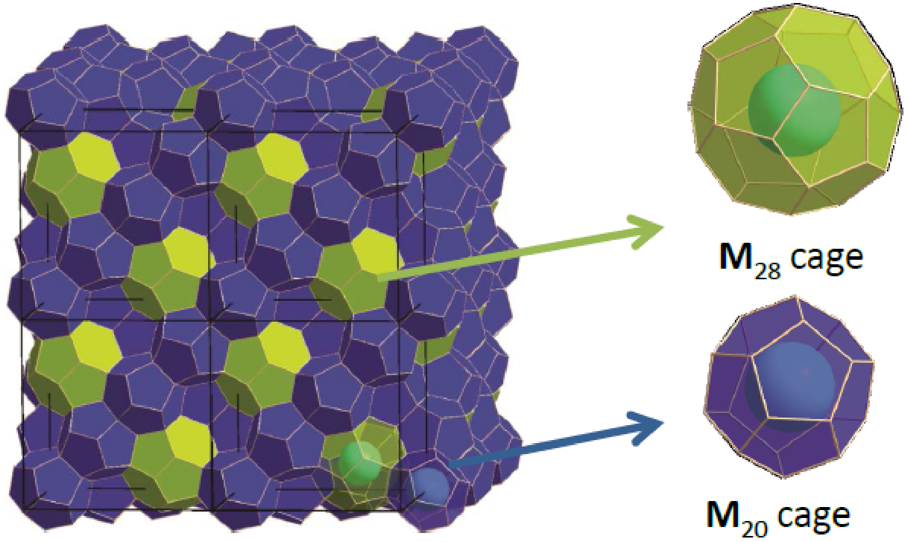
Allotropes of Silicon

Na_4Si_{24} synthesized at high pressure,
Na removed by thermal degassing,
Open framework structure – Cmcm
A quasidirect band gap 1.3 eV

Si_{136} and Ge_{136} Clathrate II Fd-3m

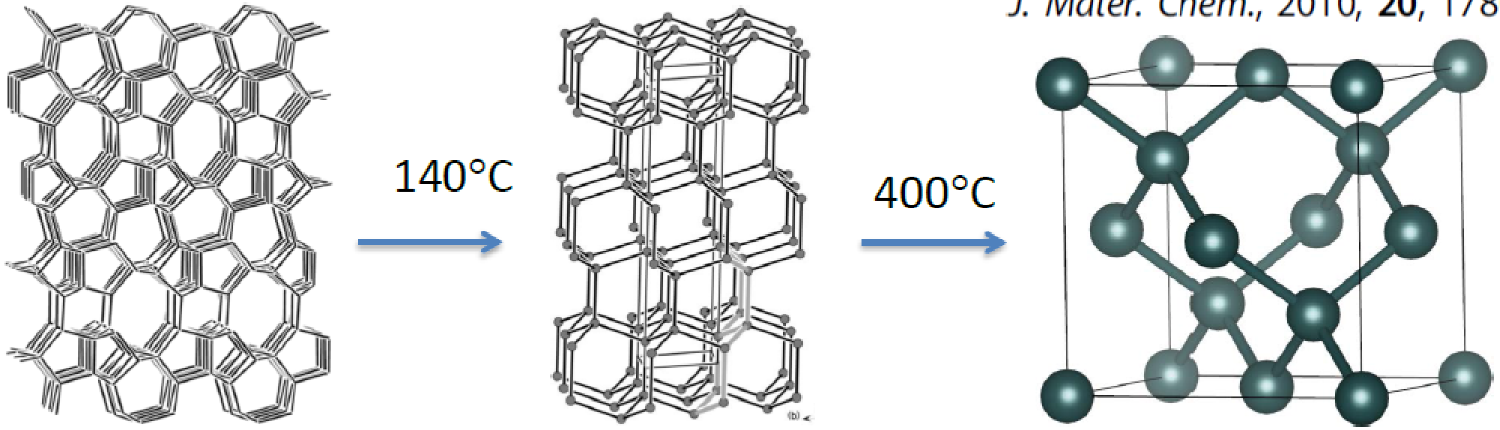
M = Si, Ge
Cages occupied by Na or K that can be removed





Allotropes of Germanium

120 kilobars, allotrope *beta*-germanium = *beta*-tin
2014, the vapor of germanium deposited on a gold surface by molecular beam epitaxy, a 2D single-layered “germanene”

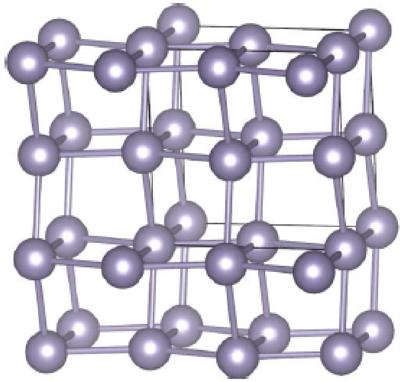


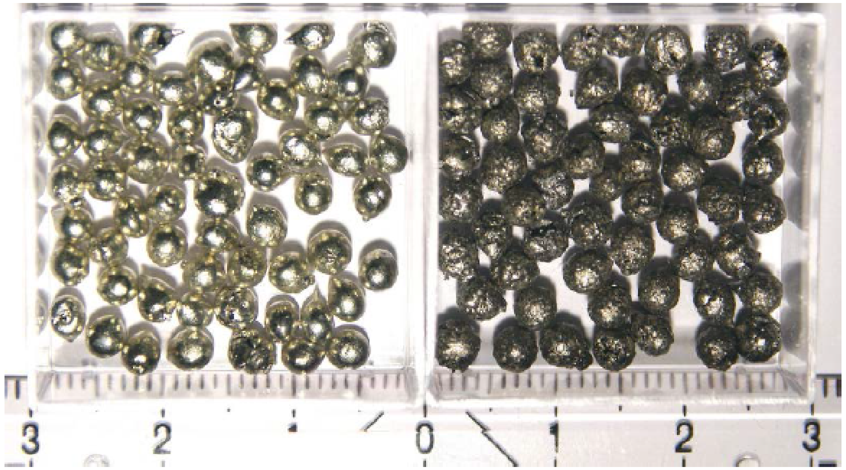
J. Mater. Chem., 2010, **20**, 1780–1786

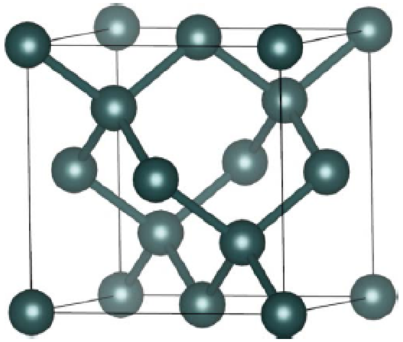
m-allo-Ge   4H-Ge ($P6_3/mmc$)   α-Ge ($Fd\text{-}3m$)

Expands as it solidifies
Semiconductor, refined to impurity concentration of only 1 part in 10^{10}

Allotropes of Tin

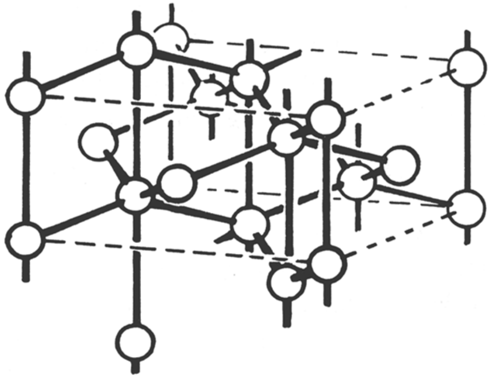

β-Sn ($I4_1/amd$)
white tin

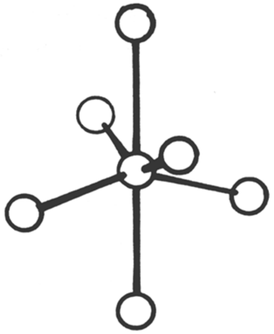



α-Sn ($Fd\text{-}3m$)
grey tin

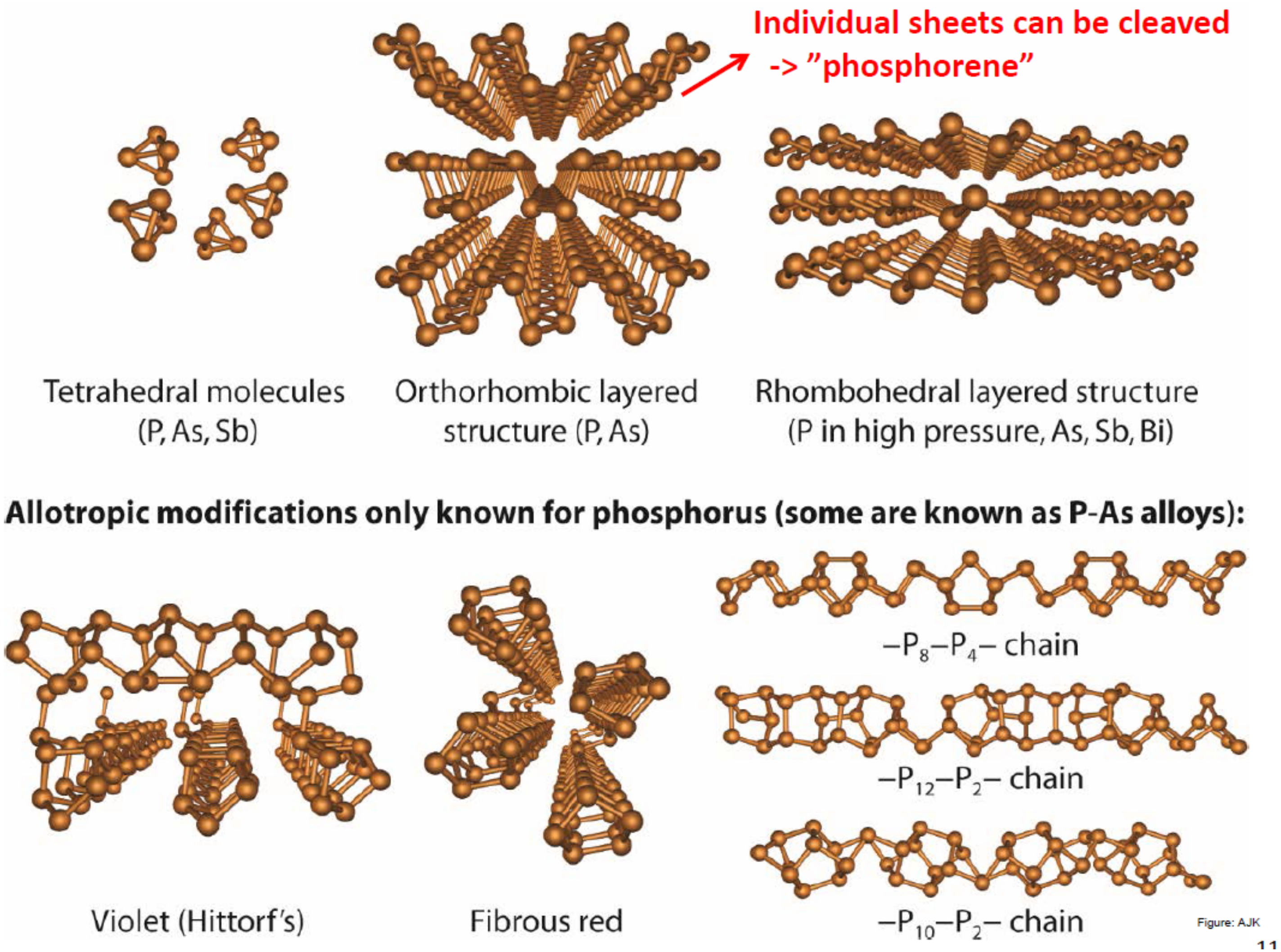
Beta White Sn (metallic)
Coordination number 6, Sn-Sn bond lengths 302 and 318 pm

Alpha Gray Sn - diamond type
stable below 13 °C, semiconductor
Coordination number 4
Sn-Sn bond length 281 pm





Allotropes of Gr15 Elements



Individual sheets can be cleaved
-> ”phosphorene”

Tetrahedral molecules
(P, As, Sb)

Orthorhombic layered
structure (P, As)

Rhombohedral layered structure
(P in high pressure, As, Sb, Bi)

Allotropic modifications only known for phosphorus (some are known as P-As alloys):

Violet (Hittorf's)

Fibrous red

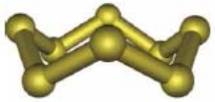
$-P_8-P_4-$ chain

$-P_{12}-P_2-$ chain

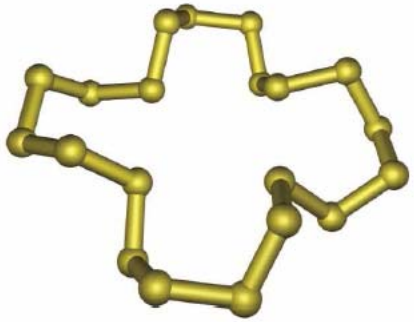
$-P_{10}-P_2-$ chain

Figure: AJK

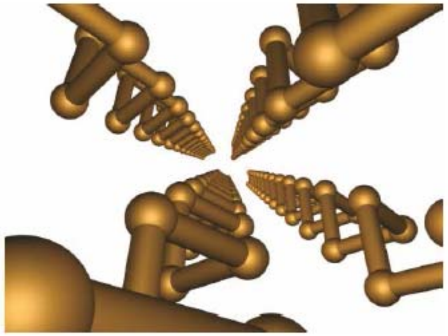
Allotropes of Gr16 Elements



α-orthorhombic cyclo-S_8



cyclo-S_{20}



gray selenium and tellurium
helical chains

Other sulfur allotropes such as 7, 9, 10, 11, 13, 14, 15, 18, and 20-membered rings have been synthesized

1930’s

Zintl Phases

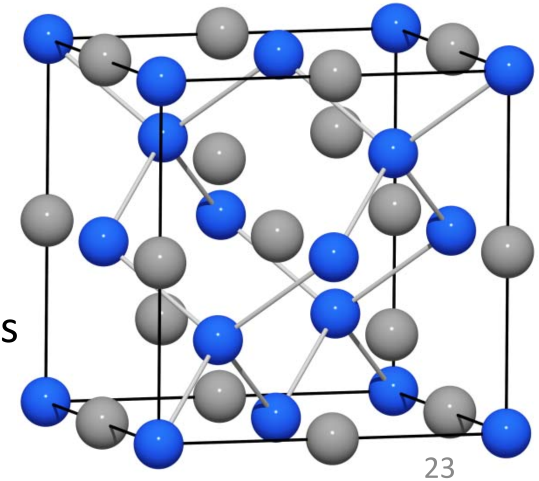
Zintl Phases = discrete charges at some intermetallic phases, valence compounds formed between the electropositive elements (alkali, alkaline-earth, and rare-earth elements) and the electronegative post-transition, main group elements (including Al, Si, P, and, to some extent, S).
Solids that can exhibit metallicity, ionicity, and covalency simultaneously.

Eduard Zintl
(1898 – 1941)

***triels* (trielides, Tr, Group 13: B - Tl)**
***tetrels* (tetrelides, Tt, Group 14: C - Pb)**
***pnicogens* (pnictides, Pn, Group 15: N - Bi)**
chalcogens (chalcogenides, Ch, Group 16, O - Po)

Zintl Boundary: separates the triels from the tetrels, different chemistry in reactions with alkali metals in liquid ammonia:

- Tetrel elements form soluble (typically highly colored) clusters
- Triel elements form insoluble, extended solids



Zintl Phases Characteristics

Compounds with fixed compositions (fixed stoichiometry)
Key concept: **isoelectronic** principle - same number of valence electrons and the same structure, i.e. number and connectivity of atoms, but different chemical composition (CO / N_2)

Stable (mono)anions of the later *p*-elements, the connectivity of the various elements follows the 8-*N* rule

- in the solid state - salt-like structures, e.g., Mg_2Si is anti-fluorite
- in solution - polyanionic clusters

typically brittle, deeply colored, semiconducting, adopting fixed compositions (no homogeneity width or little compositional variation), show large heats of formation and volumes of formation (charge-transfer effects)
some Zintl-phases are soluble in liquid ammonia (cluster anions)
- brittle (like salts)
- higher melting points than the pure metals they are build of
- semiconductors (the higher the atomic number of the electronegative part, the smaller is the bandgap of the semiconductor)

Zintl-Klemm Phases

Octet rule

the “pseudoatom” approach from Klemm

- isolated atoms will be isoelectronic with noble gases (closed shell): Sb^{3-}
- atoms in dimers will be isoelectronic with halogens: Sb_2^{4-}
- atoms in chains or rings will be isoelectronic with chalcogens: square Sb_4^{4-}
- atoms that are 3-bonded (in sheets or 3D nets) will be isoelectronic with pnicogens
- atoms that are 4-bonded (tetrahedral coordination) will be isoelectronic with tetrels

Hypervalent (not octet) linear Sb_3^{7-}

Zintl Phases - Synthesis

Syntheses of Zintl-phases

a) reduction in **liquid ammonia** (titration of PbI_2 with Na solution)

$$22\ Na + 9\ PbI_2 + n\ NH_3\ (l) \rightarrow Na_4Pb_9 \cdot nNH_3 + 18\ NaI$$

b) direct **solid state** reaction

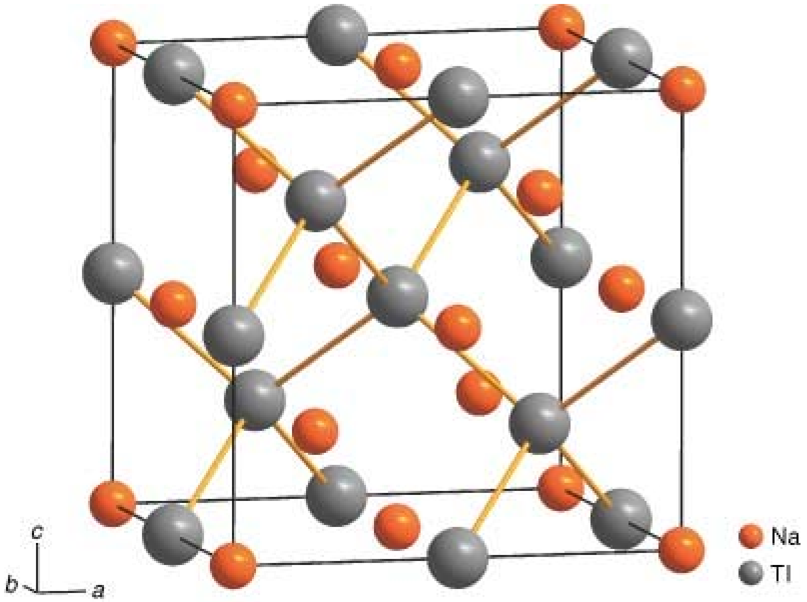
$$Ca + Si \rightarrow CaSi$$

c) cathodic decomposition - binary compound is decomposed at the cathode and polyanions go into solution

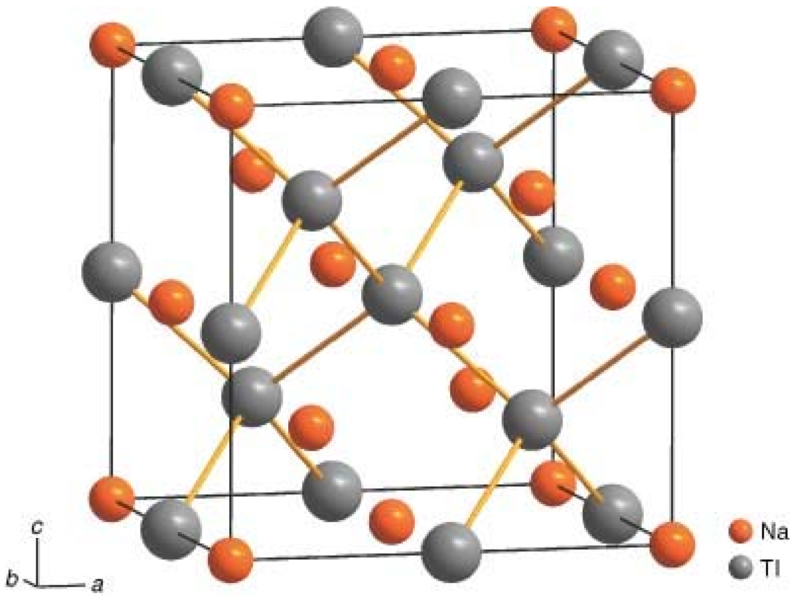
Zintl-Klemm Phases

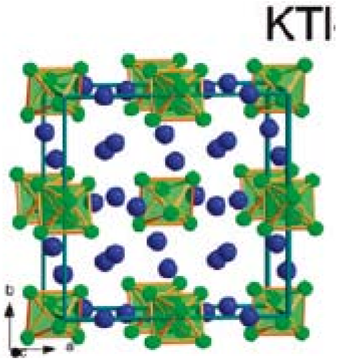
Wilhelm Klemm expanded the concept to the “pseudoatom” approach:
polyanions look like a following element.

NaTl is the protoptype Zintl phase. NaTl is formulated as $Na^+ Tl^-$, and Tl^- adopts a structure like Si, Ge or Sn (one element to the right, but NOT Pb!).
Na donates its 3s electron to Tl, resulting in a formal Tl anion with 4 valence electrons. This “anion” behaves as a pseudotetrel atom, each of which forms 4 covalent bonds and adopts the diamond structure.
Each Na^+ “cation” acts as a charge balancer and space filler.



Zintl-Klemm Phases





Na and Tl form sublattices - independent interpenetrating diamond networks.
The atoms sit on the sites of a bcc lattice with $a_{bcc} = ½ a$.

Each Na atom is surrounded by 4 Na atoms arranged tetrahedrally and 4 Tl atoms arranged tetrahedrally. Together the 8 surrounding atoms form a cube. Each Tl atom is similarly surrounded by 4 Tl atoms and 4 Na atoms forming a cube. Four of each type of cube combine to make the unit cell, smaller cube having sodium atom at its center

NaTl a = 749 pm Space group Fd3m (227)

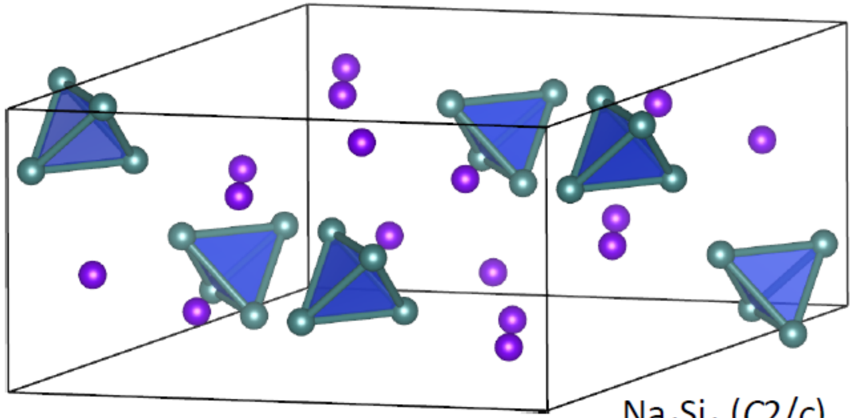
LiAl, LiGa, and LiIn form NaTl structure, KTl and contains Tl_6 distorted octahedra while LiTl adopts a CsCl-type structure.

Zintl-Klemm Phases

NaSi (Na_4Si_4)

each Na atom donates 1e–
each Si atom accepts 1e–

Si_4^{4-} tetrahedra are isoelectronic with P_4 tetrahedra (white phosphorus)

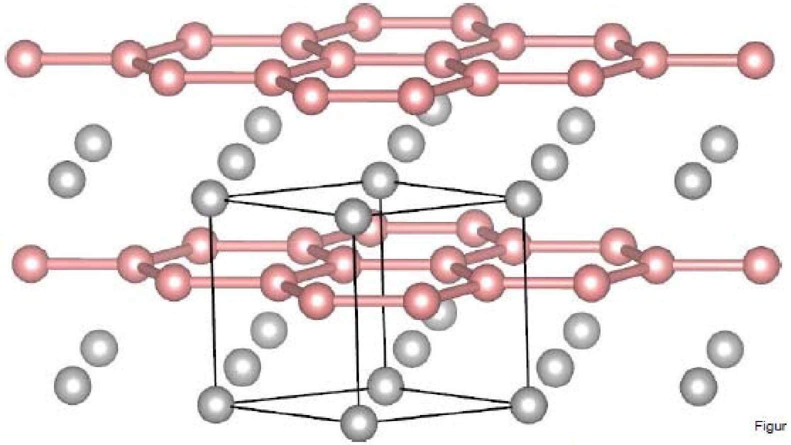


Na_4Si_4 ($C2/c$)

MgB_2

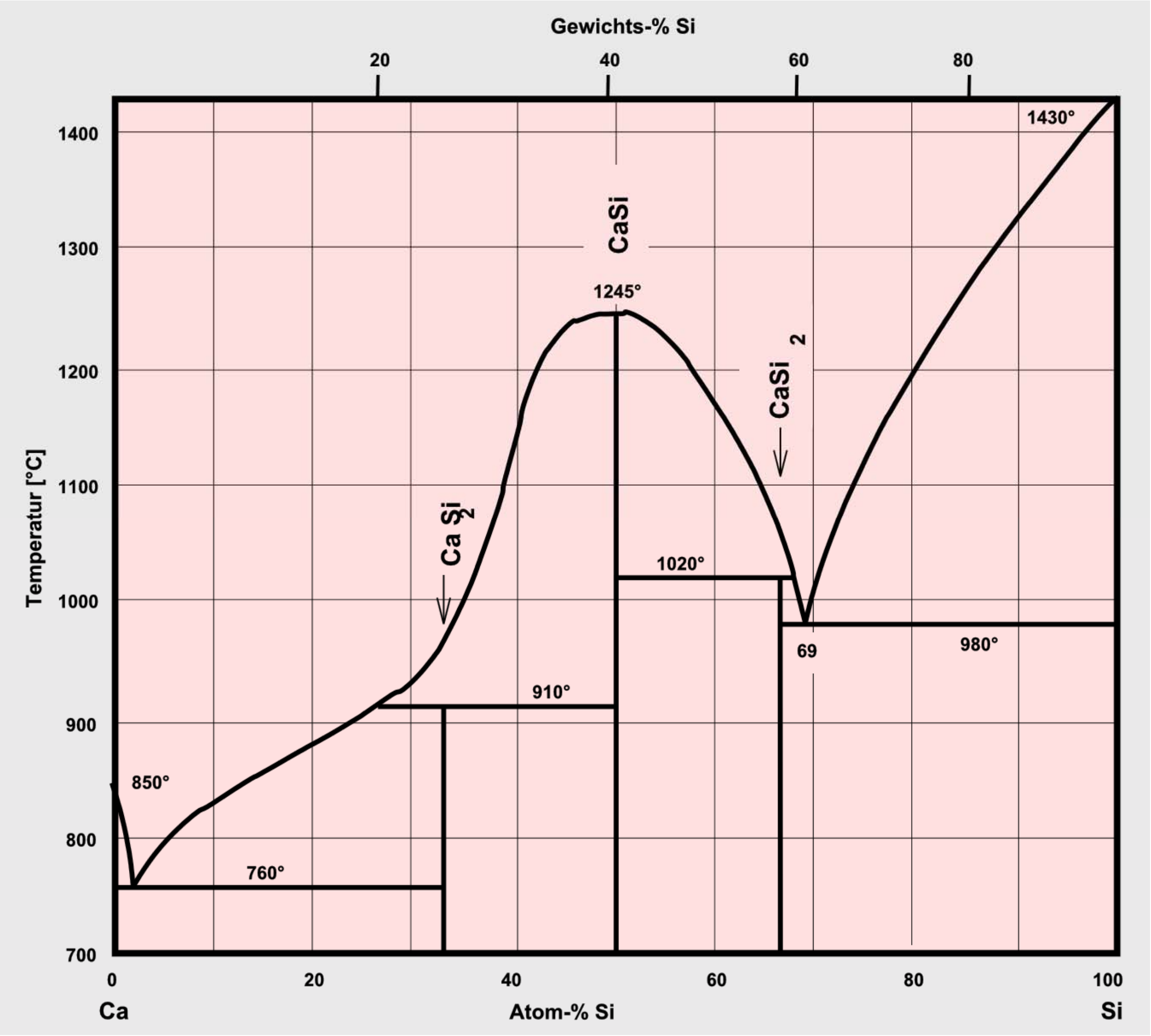
each Mg atom donates 2e–
each B atom accepts 1e–

Two-dimensional B network isoelectronic with graphene



MgB_2 ($P6/mmm$)

Zintl-Klemm Phases

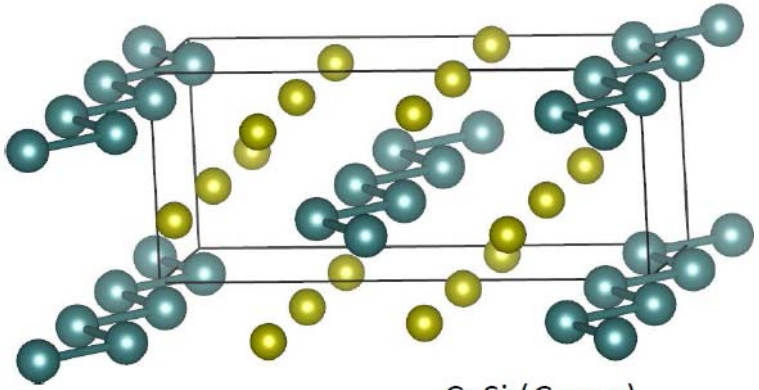


Zintl-Klemm Phases

CaSi

each Ca atom donates2e^{-}
each Si atom accepts 2e^{-}

The resulting one-dimensional Si-chains are related to S/Se/Te -chains
(but planar, not helical)

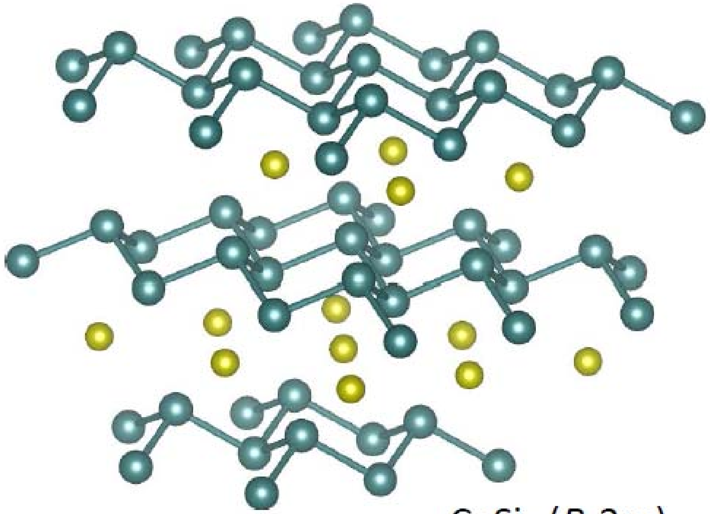


CaSi (*Cmcm*)

$\mathrm{CaSi_2}$

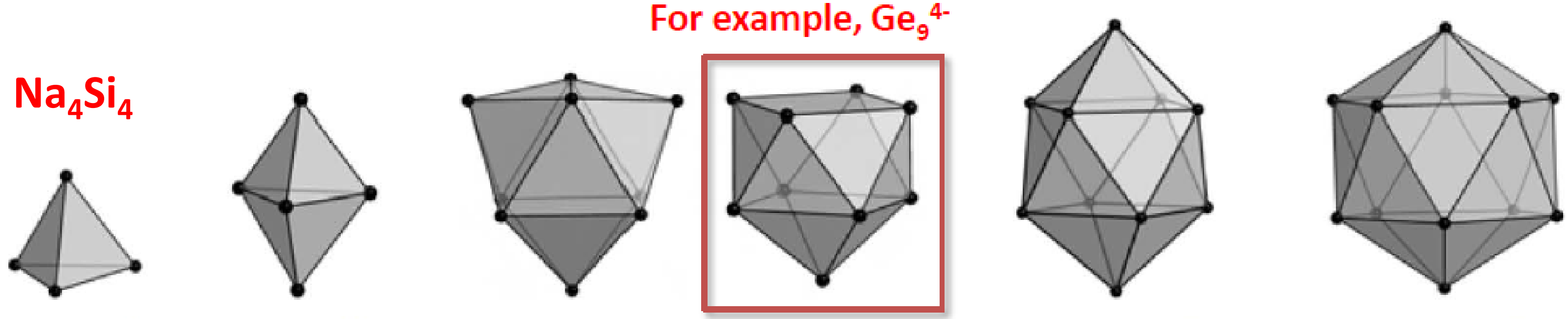
each Ca atom donates 2e^{-}
each Si atom accepts 1e^{-}

The resulting two-dimensional Si-network is isoelectronic and structurally analogous with As/Sb/Bi



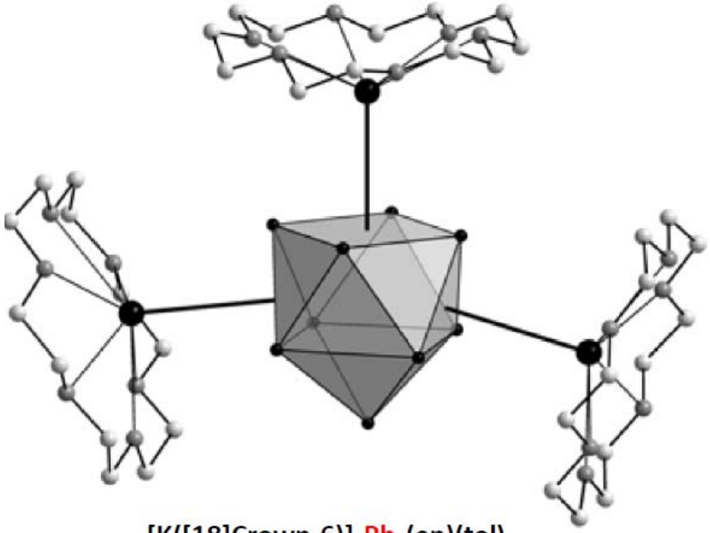
$\mathrm{CaSi_2}$ (*R*-3*m*)

Zintl-Klemm Phases

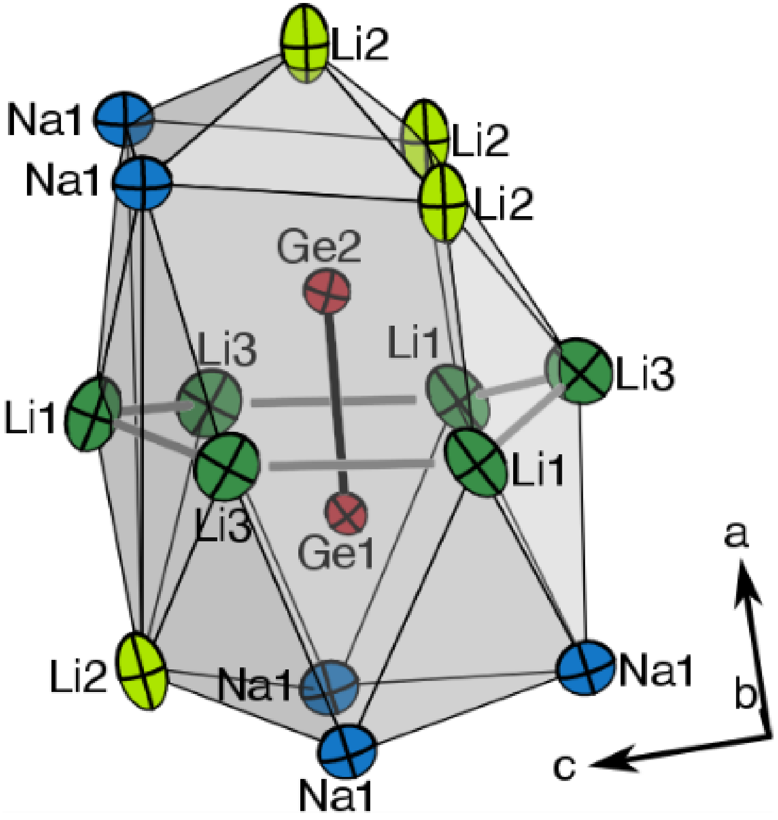

Na_4Si_4

For example, Ge_9^{4-}

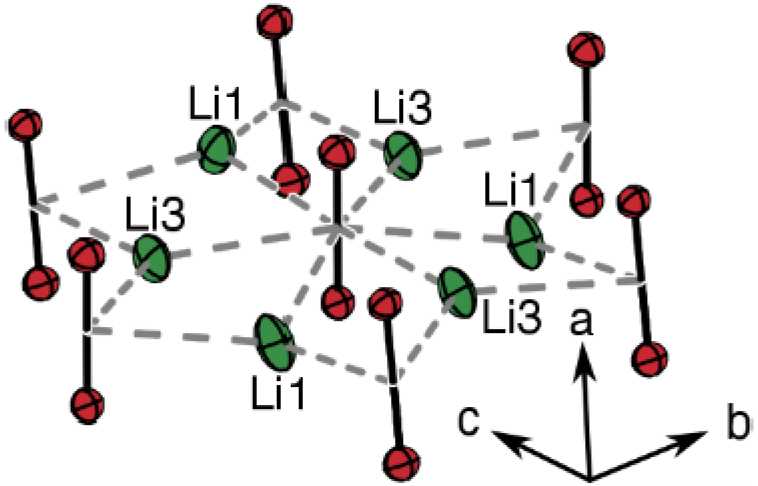
(a) $[E_4]^{4-}$ (b) $[E_5]^{2-}$ (c) $[E_9]^{x-}$ (d) $[Pb_{10}]^{2-}$ (e) $[E_{12}]^{2-}$


$[K([18]Crown\text{-}6)]_4Pb_9(en)(tol)$

$[Ge_2]^{4-}$ in the Zintl Phase Li_3NaGe_2



$(Li^+)_3(Na^+)[Ge_2]^{4-}$



T. F. Faessler et al., Angew 2016, 55, 1075

How to Characterize the $[Ge_2]^{4-}$ Double-Bond ?

Bond distance Ge=Ge

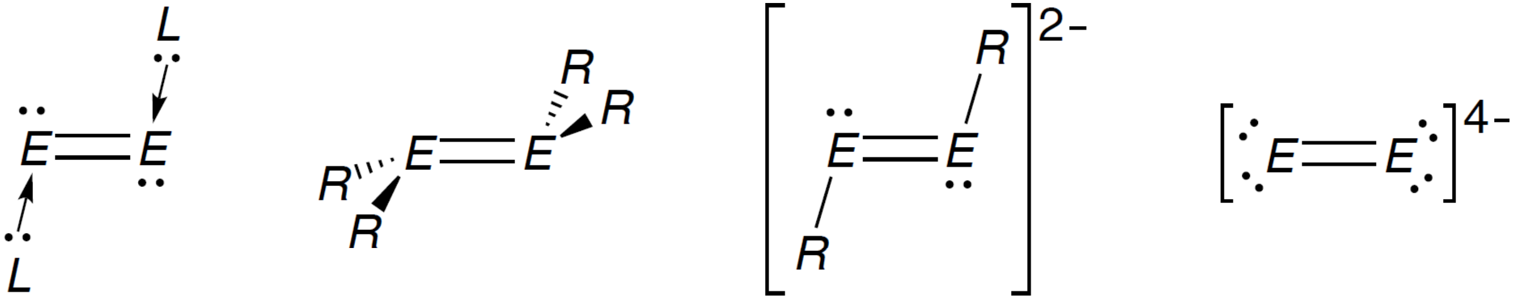
Raman spectroscopy – Ge=Ge stretching

^{6}Li NMR spectroscopy – chemical shift of coordinated lithium atoms Li1/Li3

MO calculation

Band structure calculation

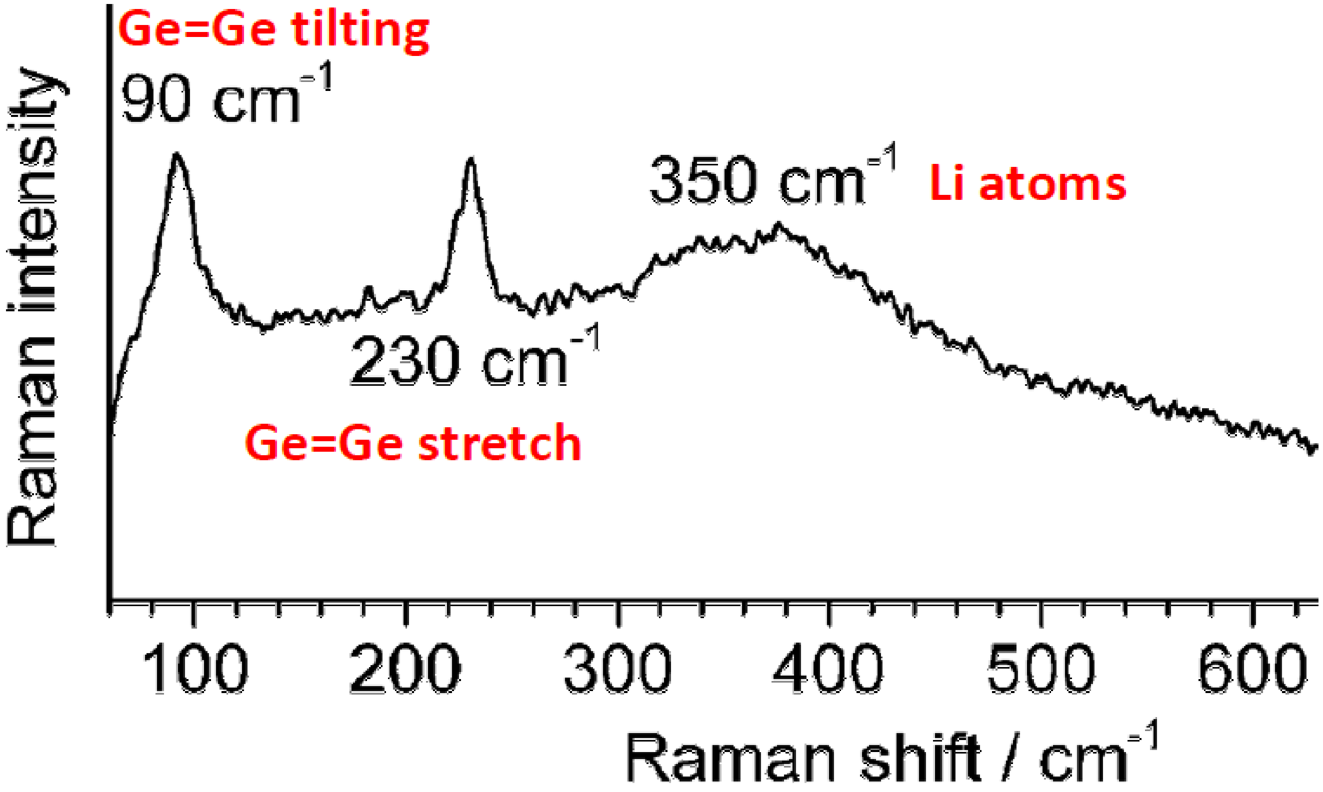
Bond Lengths in E=E (Si and Ge)



E = Si	2.23 Å[14a]	2.14-2.29 Å[2]	-	(≥ 2.34 Å[15])
E = Ge	2.35 Å[14b]	2.21-2.51 Å[2]	2.39-2.46 Å[6]	(≥ 2.44 Å[10])

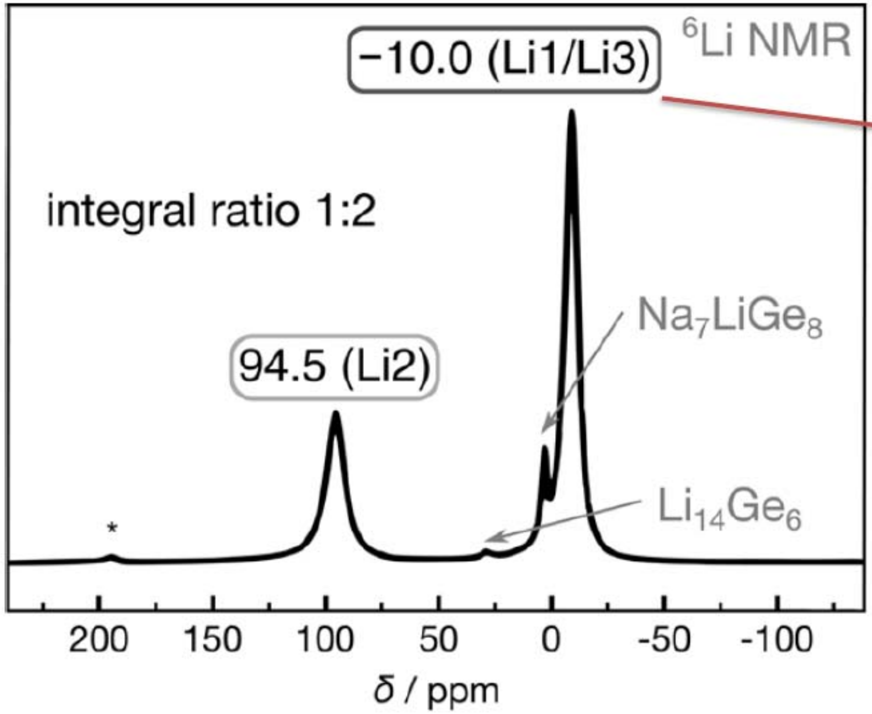
$[Ge_2]^{4-}$ bond distance in Li_3NaGe_2	2.390(1) Å
Ge–Ge bond distance in bulk α-Ge	2.45 Å

Raman Spectrum of a Li_3NaGe_2 Single Crystal

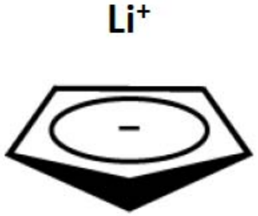


Assignment of the modes: Quantum chemical calculations

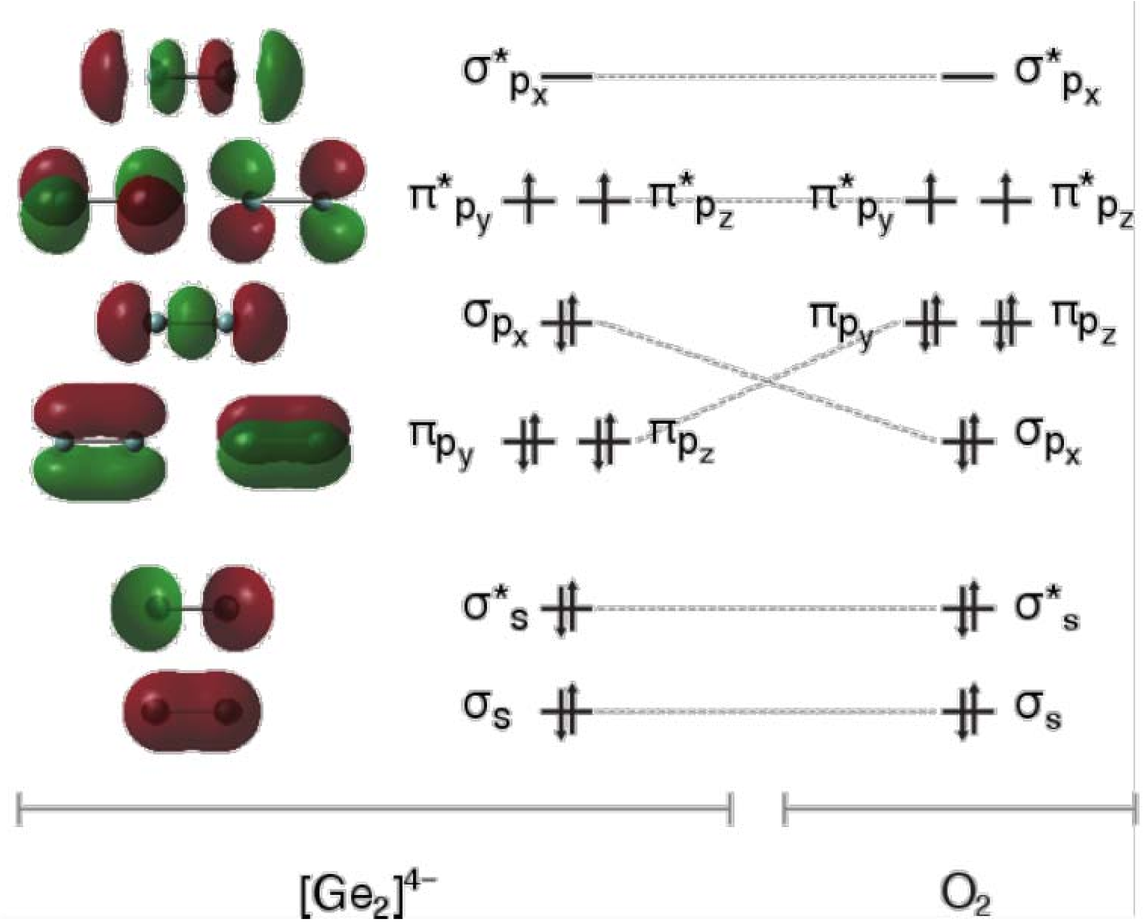
^{6}Li NMR on Li_3NaGe_2



Negative shift, similar to π-coordinated Li^+ in for example (Li^+)(Cp^-) with –7.6 ppm

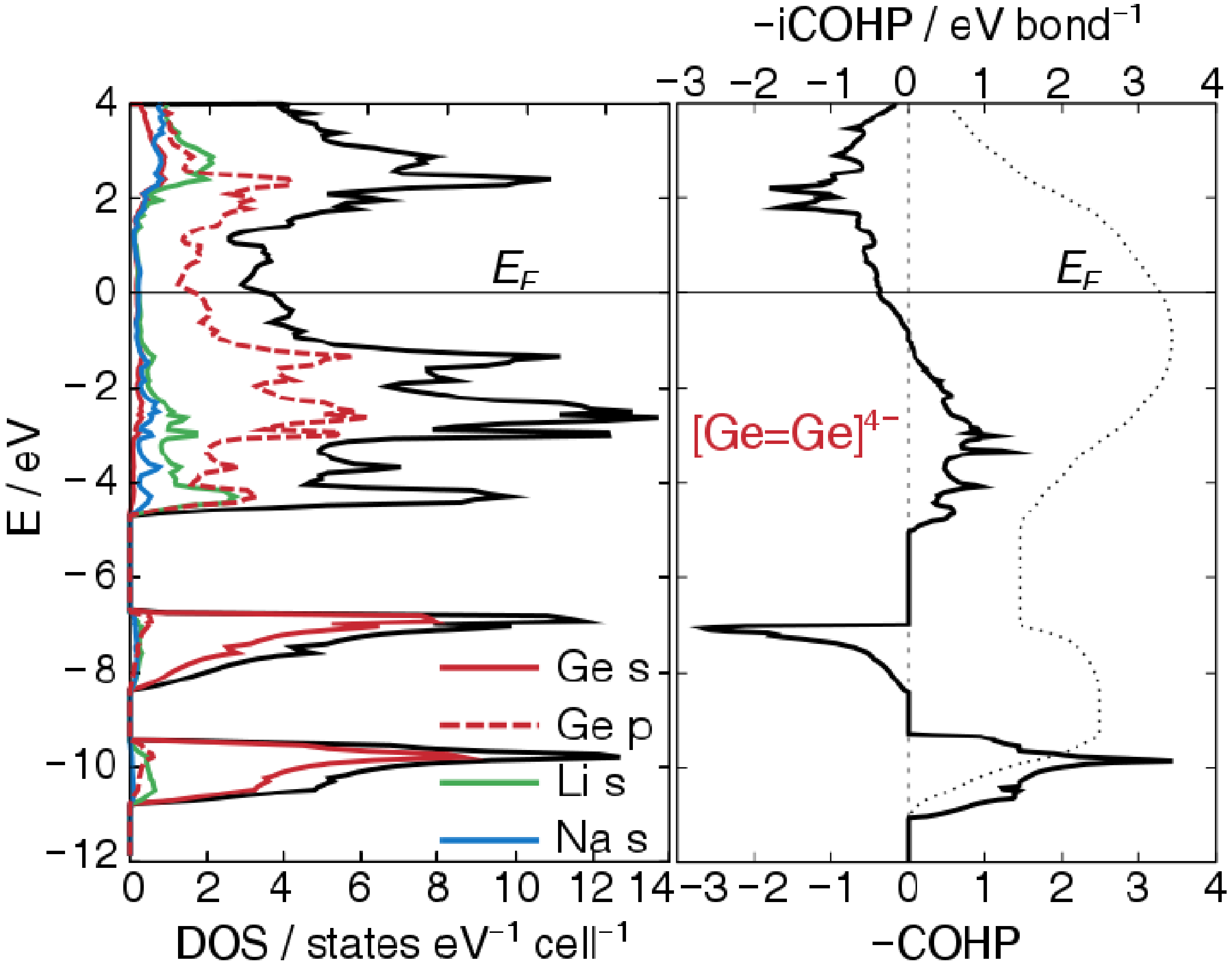


Molecular Orbitals of $[Ge_2]^{4-}$ and O_2



$[Ge_2]^{4-}$ = a solid-state equivalent to O_2

Band Structure Analysis



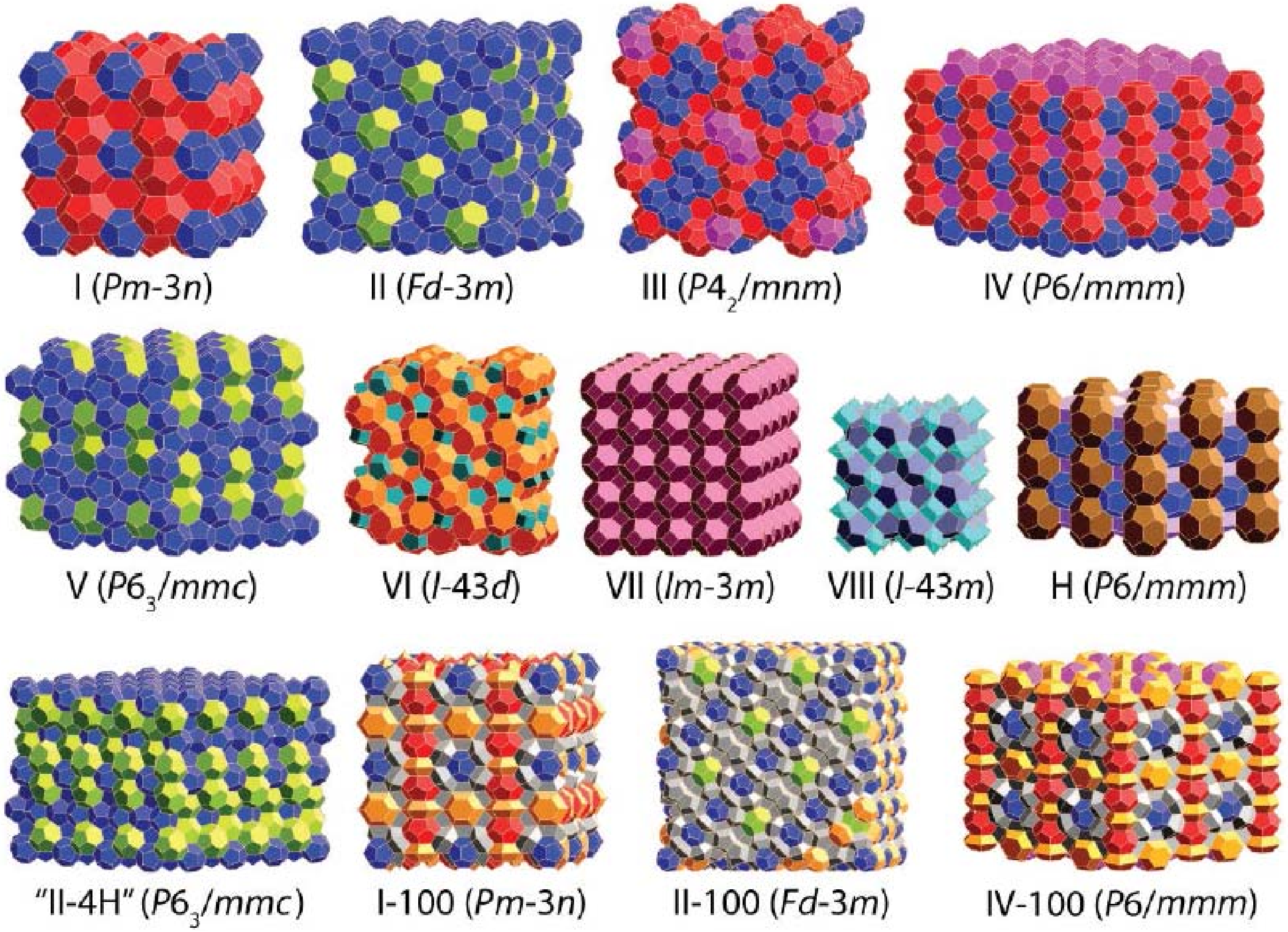
Unoccupied bands

Fermi level

Occupied bands

metallic (conducting) solid

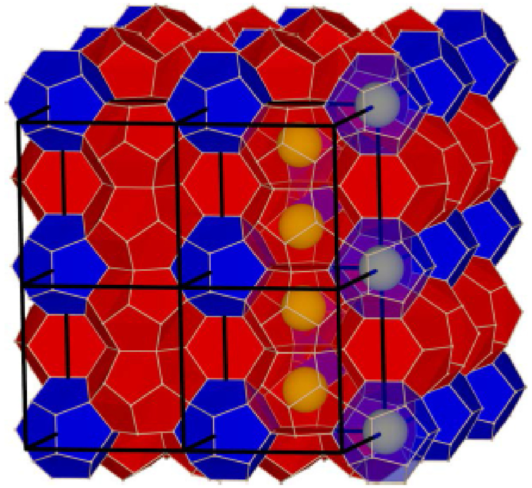
Clathrate Frameworks



Zintl Phases Semiconducting Gr14 Clathrates

Charge transfer occurs between the guest and the framework

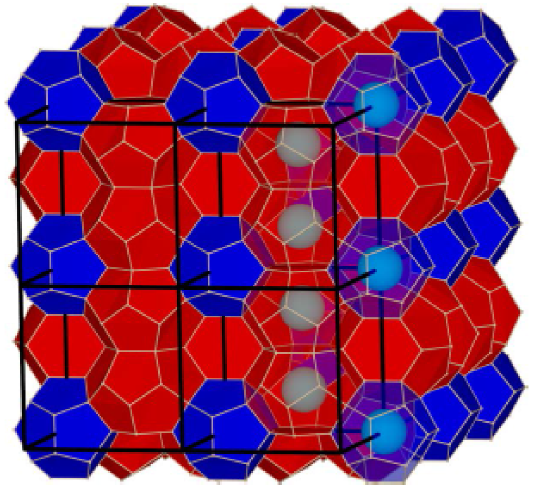
Clathrate-I (*Pm*-3*n*, 46 framework atoms in the unit cell)



$Ba_8[Ga_{16}Ge_{30}]$

each Ba atom donates $2e^-$
each Ga atom accepts $1e^-$

Ga and Ge forms 4-coordinated frameworks



$I_8[As_8Ge_{38}]$

each I atom accepts $1e^-$
each As atom donates $1e^-$

As and Ge forms 4-coordinated frameworks

Polyhedral Cages

A large family of polyhedral molecules

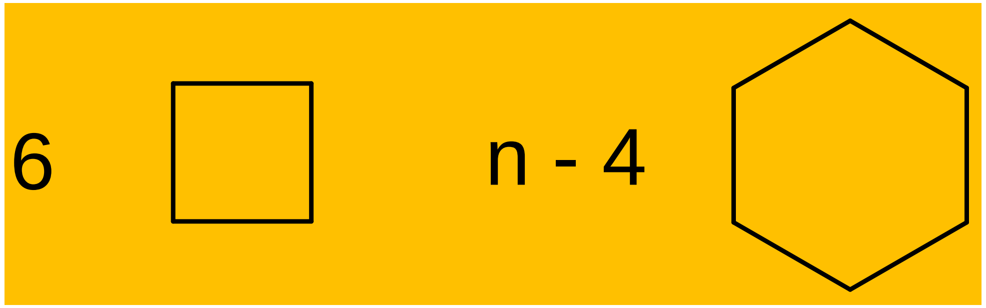
Follow **Smith's Rule**
n = degree of aggregation (4 to 12)

Contain 6 squares and n – 4 hexagons

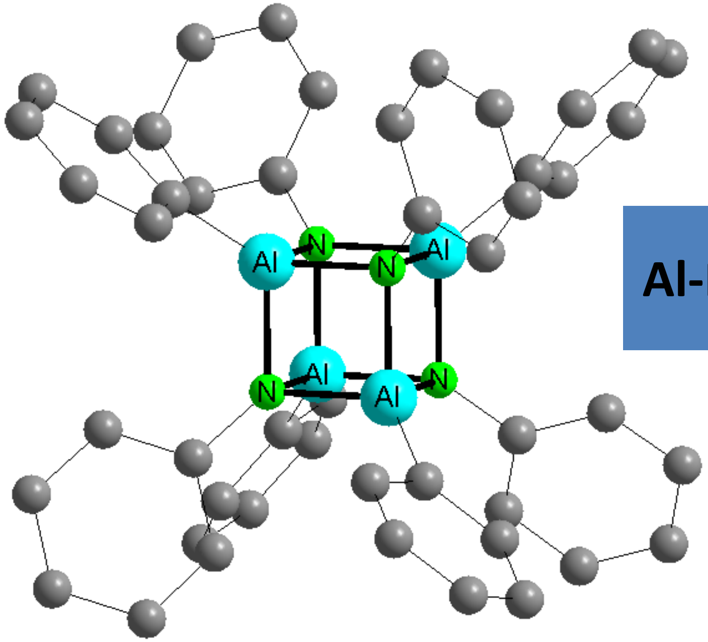
Both M and E centers are four-coordinate for Al and N, three-coordinate for O

Iminoalanes $[\mathrm{R\text{-}Al{=}N\text{-}R'}]_n$

Alumoxanes $[\mathrm{R\text{-}Al{=}O}]_n$

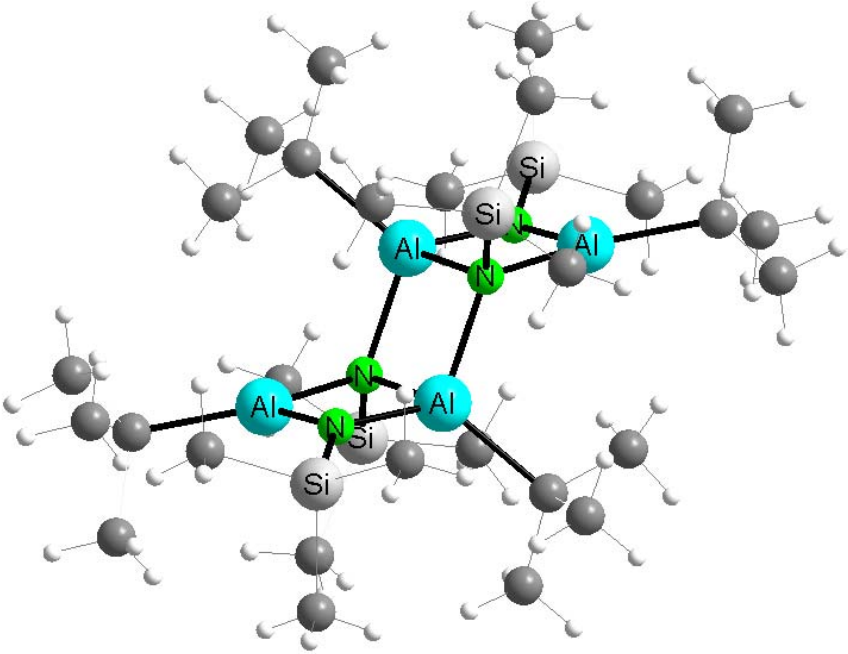


Polyhedral Cages n = 4



n = 4

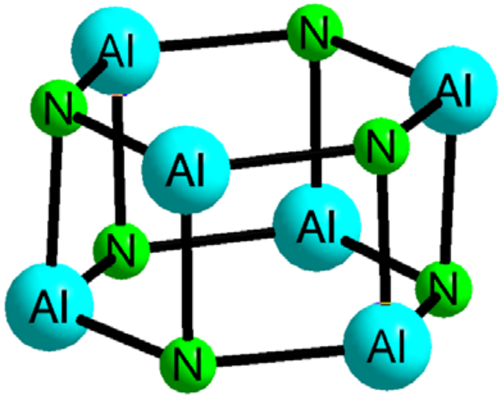
Al-N 1.95 Å



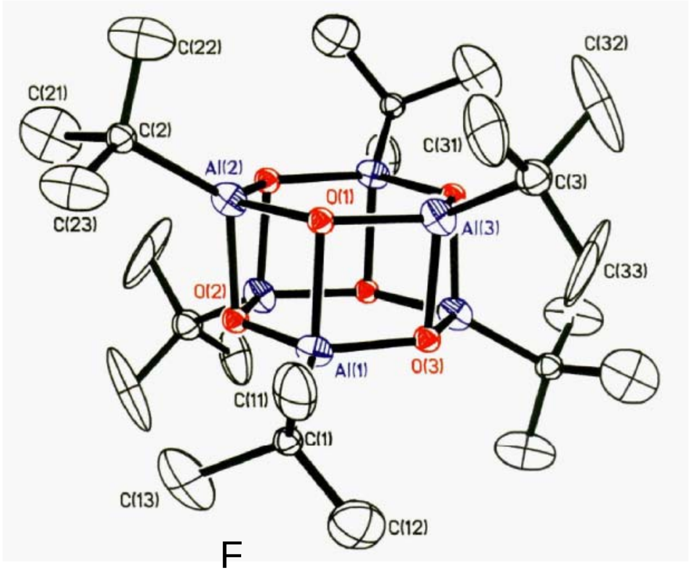
n = 4
What is wrong?

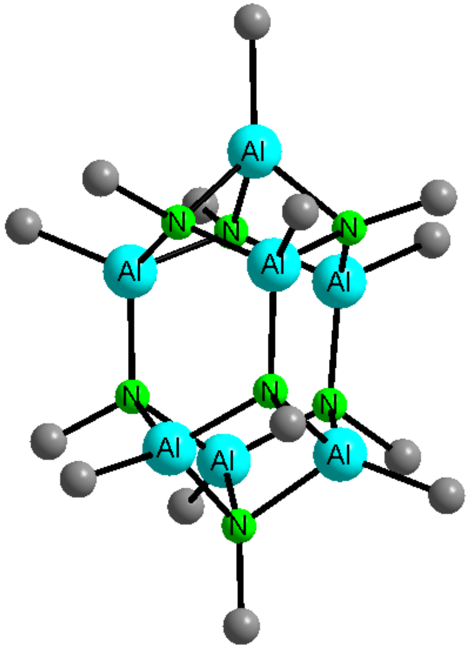
No polyhedron known for n = 5 that would obey Smith's Rule

Polyhedral Cages n > 4

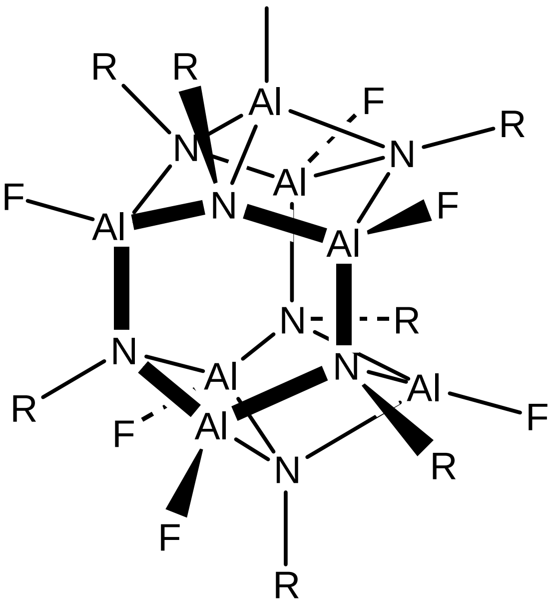


n = 6

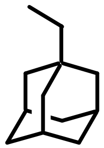




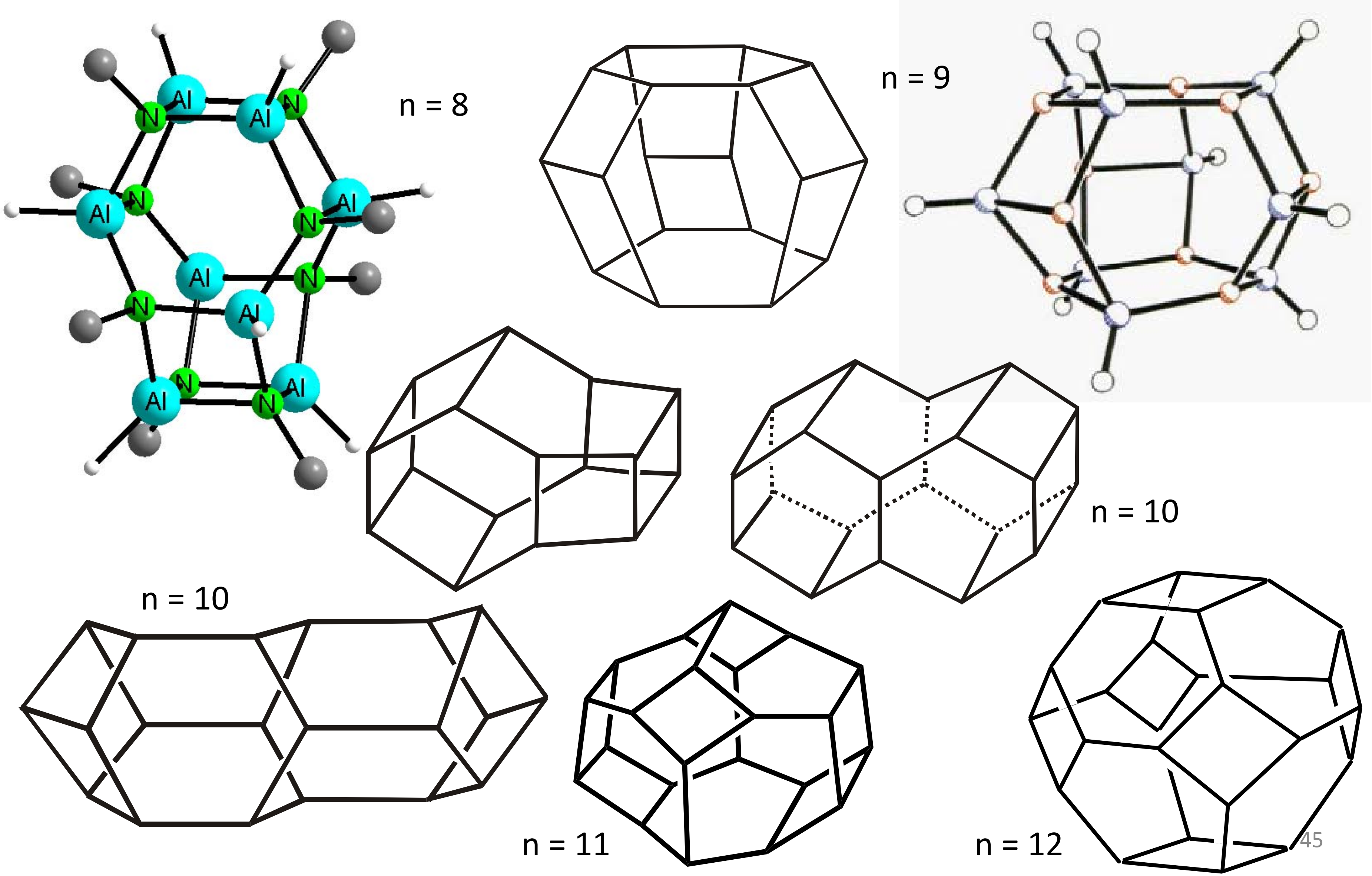
n = 7



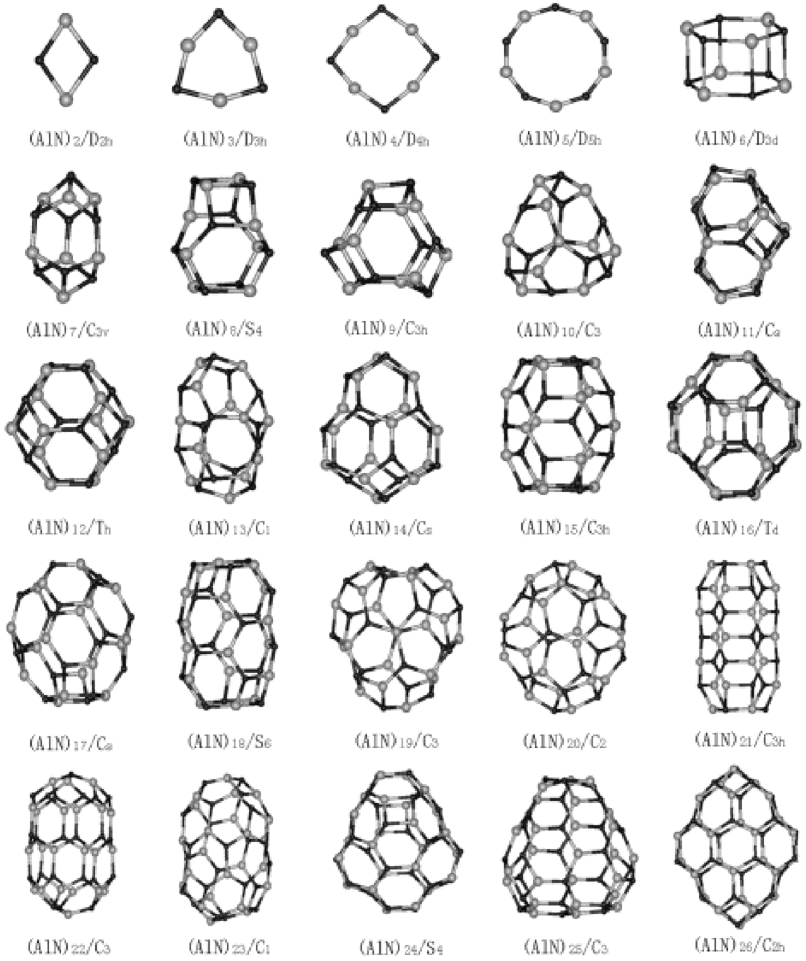
R =

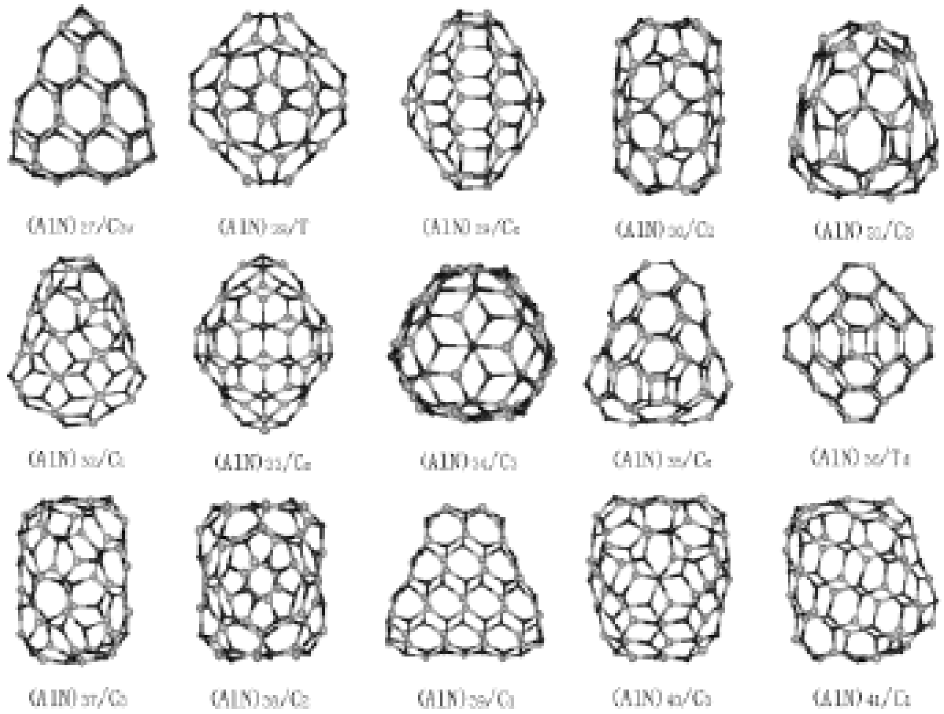


Iminoalanes $[RAlNR']_n$ n > 4



Most stable (AlN)*n* cages (*n* = 2-41)





Sphericity

Sphericity σ = a ratio of a polyhedron surface to the volume of a sphere of equal volume

V_P = polyhedron volume
A_P = polyhedron surface

$$\sigma = \sqrt[3]{\frac{36\pi V_P^2}{A_P^3}}$$

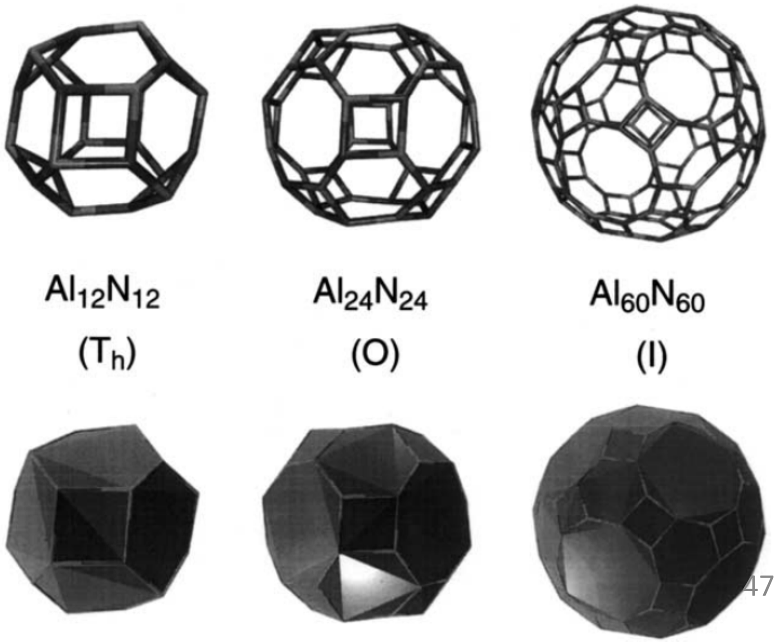
σ = 0 - 1

Sphere: σ = 1

Truncated octahedron: σ = 0.909918
$Al_{12}N_{12}$: σ = 0.944751

Truncated icosahedron: σ = 0.966622
C_{60}: σ = 0.966819
Two C-C bond lengths: 1.4584, 1.4011 Å

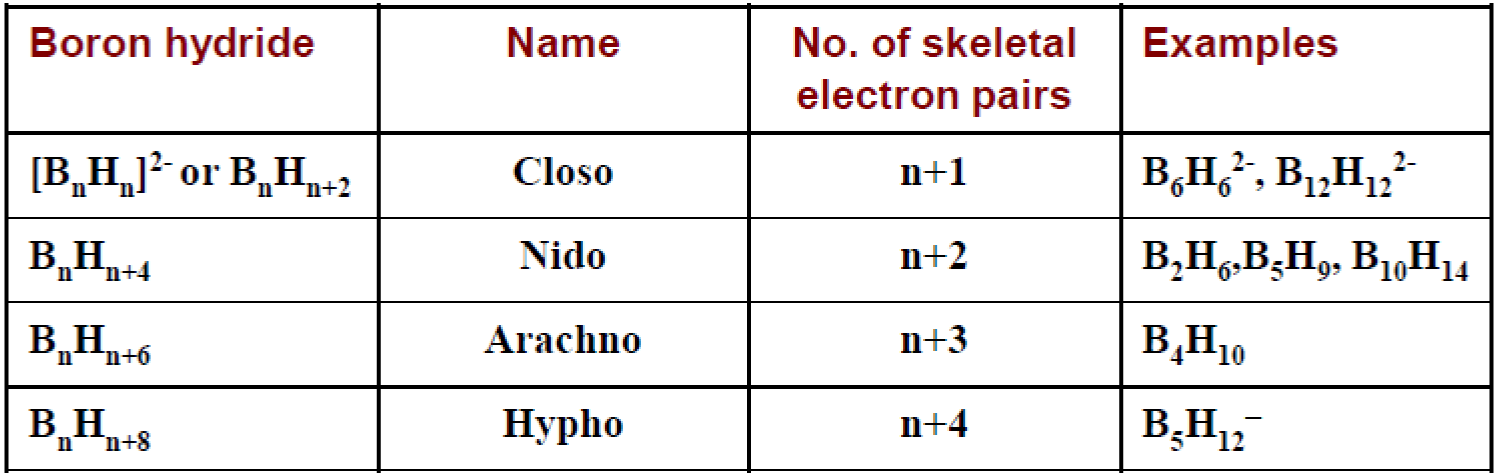
Distortion brings more sphericity



Wade’s Rules

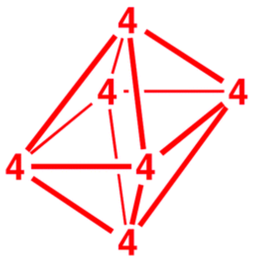
Kenneth Wade
1913-2014
Durham University UK
formulated rules which provide qualitative understanding of the electron deficient multicentre bonding of boron hydrides and their shape based classification

Wade’s rule - a cage molecule with a geometry based on a deltahedron (closed polyhedron constructed of triangles = Δ) with *n* vertices will possess *n* + 1 skeletal bonding electron pairs

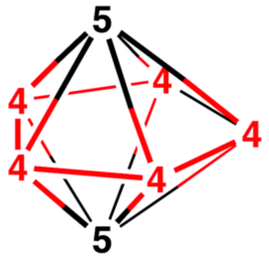


Boron hydride	Name	No. of skeletal electron pairs	Examples
$[B_nH_n]^{2-}$ or B_nH_{n+2}	Closo	n+1	$B_6H_6^{2-}$, $B_{12}H_{12}^{2-}$
B_nH_{n+4}	Nido	n+2	B_2H_6,B_5H_9, $B_{10}H_{14}$
B_nH_{n+6}	Arachno	n+3	B_4H_{10}
B_nH_{n+8}	Hypho	n+4	$B_5H_{12}^{-}$

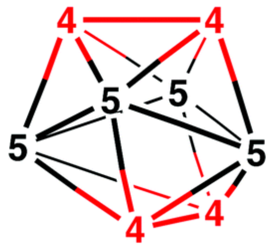
Deltahedra



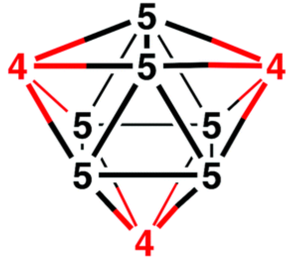
6 vertices:
Octahedron



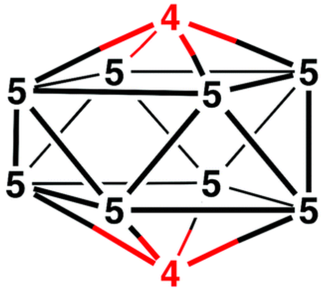
7 vertices:
Pentagonal
Bipyramid



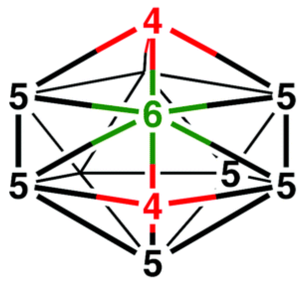
8 vertices:
Bisdisphenoid
(“D_{2d} Dodecahedron”)



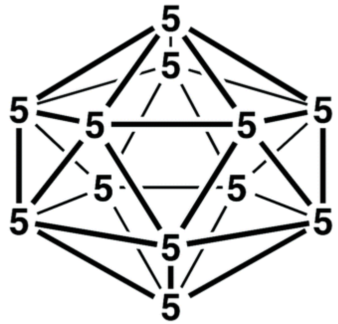
9 vertices:
4,4,4-Tricapped
Trigonal Prism



10 vertices:
4,4-Bicapped
Square Antiprism



11 vertices:
Edge-coalesced
Icosahedron

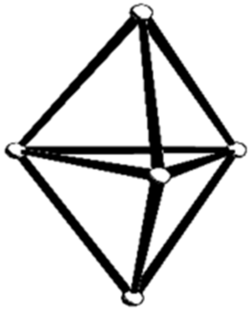


12 vertices:
Icosahedron

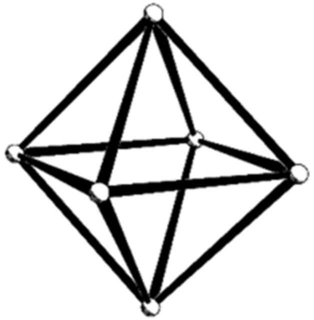
Euler’s rule: $f + v = c + 2$

f = faces, v = vertices, c = connections (bonds)

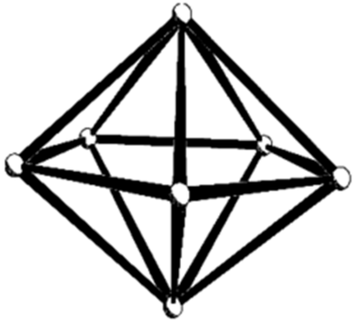
Deltahedral Boranes



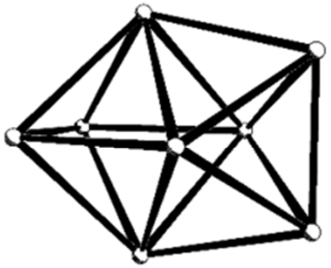
$[B_5H_5]^{2-}$, **1**



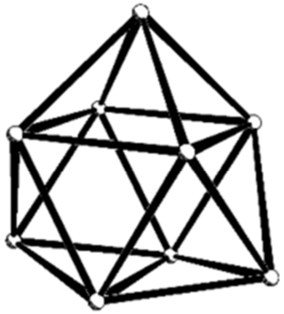
$[B_6H_6]^{2-}$, **2**



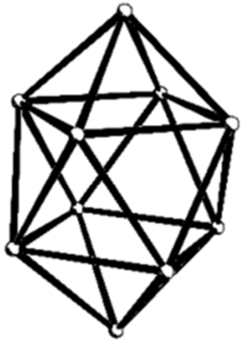
$[B_7H_7]^{2-}$, **3**



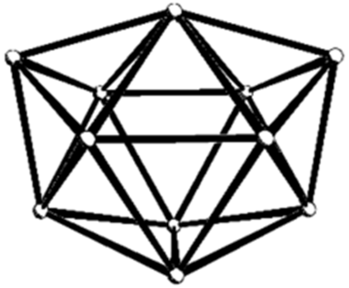
$[B_8H_8]^{2-}$, **4**



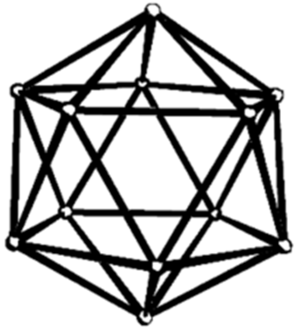
$[B_9H_9]^{2-}$, **5**



$[B_{10}H_{10}]^{2-}$, **6**



$[B_{11}H_{11}]^{2-}$, **7**



$[B_{12}H_{12}]^{2-}$, **8**

Electron deficient molecules

Lines connecting B-B pairs are not 2e-bonds

- Exoskeletal B-H bonds
- Endoskeletal bonding:

n axial orbitals combine to
1 bonding MO and n–1
antibonding MO

2n tangential orbitals combine to
n bonding and n antibonding or
nonbonding MO

n + 1 bonding MO
2n + 2 **skeletal bonding electrons**

Wade’s Rules

Determine the number of **skeletal electron pairs** in a cluster

Number of **skeletal bonding electrons** contributed by a main group atom:

$$E = v + x - 2$$

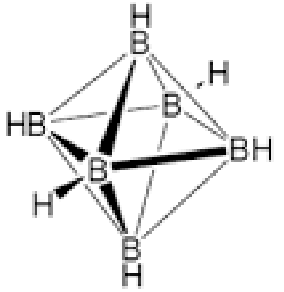
v = number of valence elctrons
x = number of electrons from ligands: Cl, F, H = 1, Lewis base = 2

Each **BH** unit furnishes **2 skeletal bonding electrons**
each B gives three, each C-H unit of a carborane furnishes 3 and each additional H· furnishes 1 skeletal bonding electron
Ionic charges must be included in the electron count

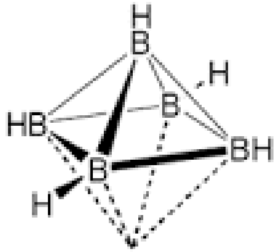
Borane clusters with hetero-elements: replace C, Si, Ge and Sn of a cluster with a BH unit; N, P and As with a BH_2 unit and S and Se with a BH_3 unit for counting purposes

Wade’s Rules

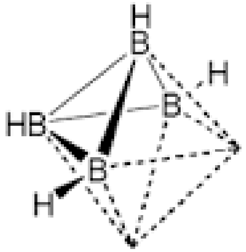
Wade’s rule states that a cage molecule with a geometry based on a closed polyhedron constructed of triangles with *n* vertices will possess *n* + 1 skeletal bonding electron pairs.



closo structure



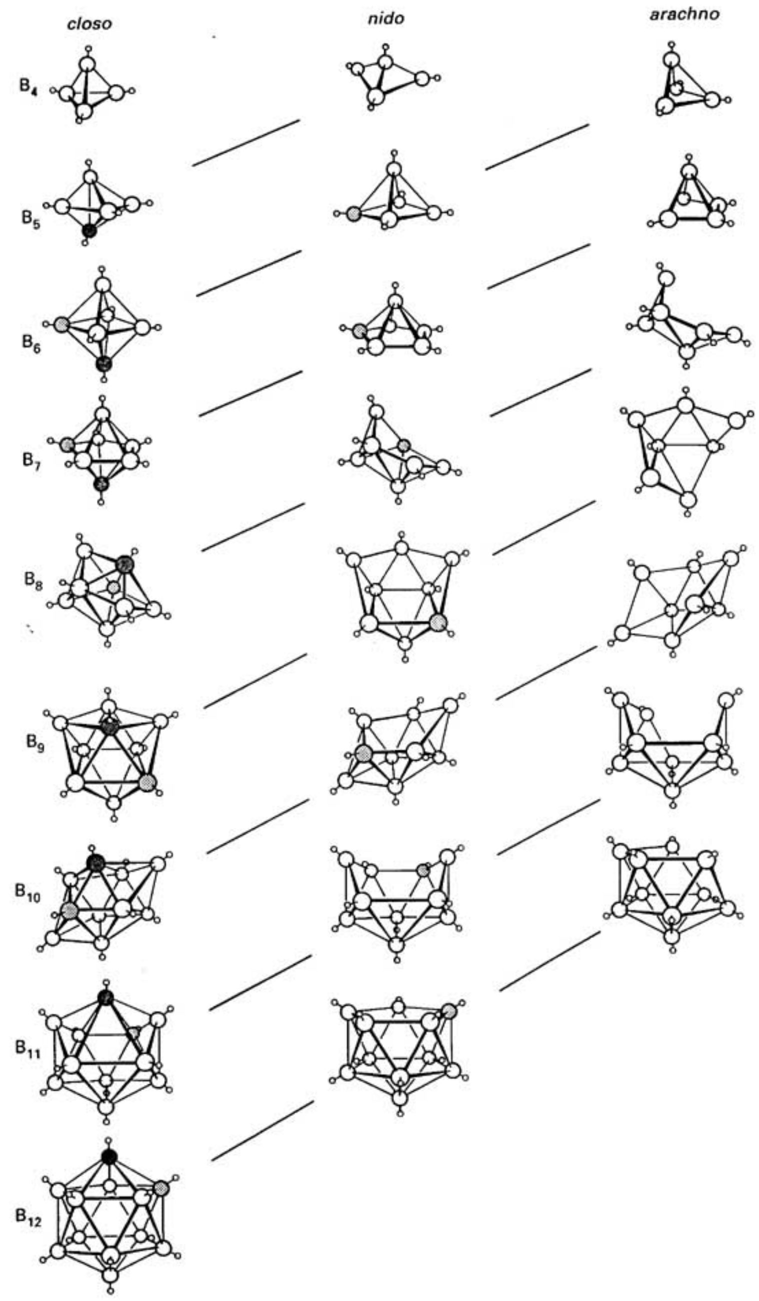
nido structure



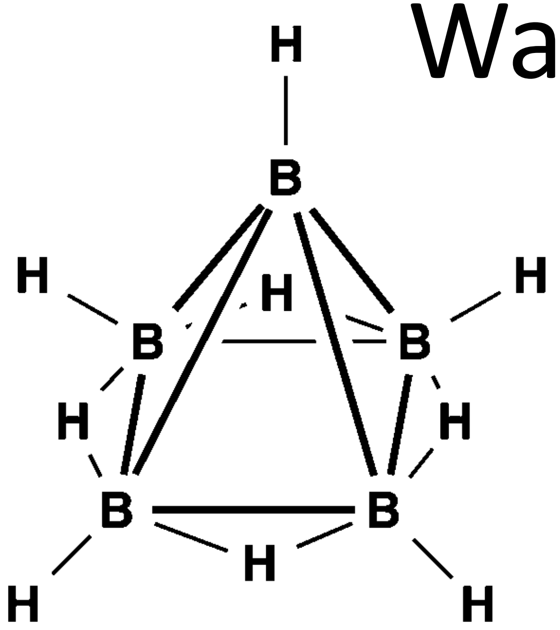
arachno structure

Closo to Nido: remove vertex of **highest order** – highest connectivity atom

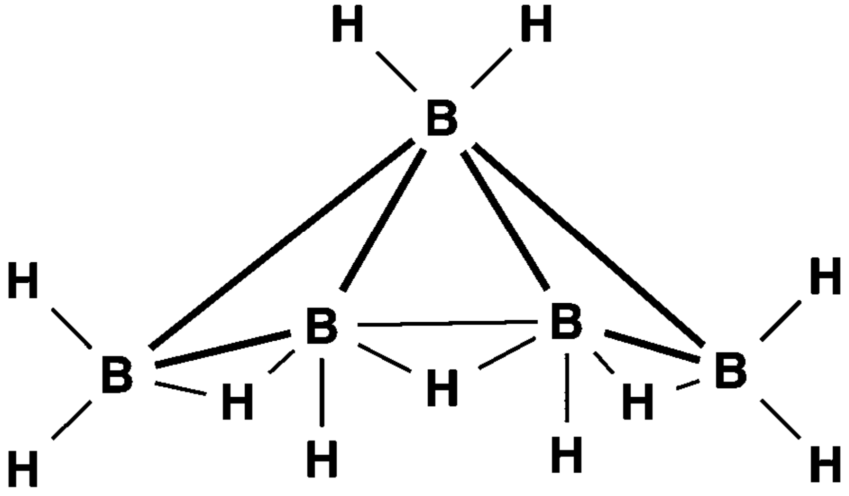
Nido to Arachno: remove vertex of **highest order** on an **open face** to generate minimum number of vertices of order 2


closo
nido
arachno
B4
B5
B6
B7
B8
B9
B10
B11
B12

Wade’s Rules



B_5H_9



B_5H_{11}