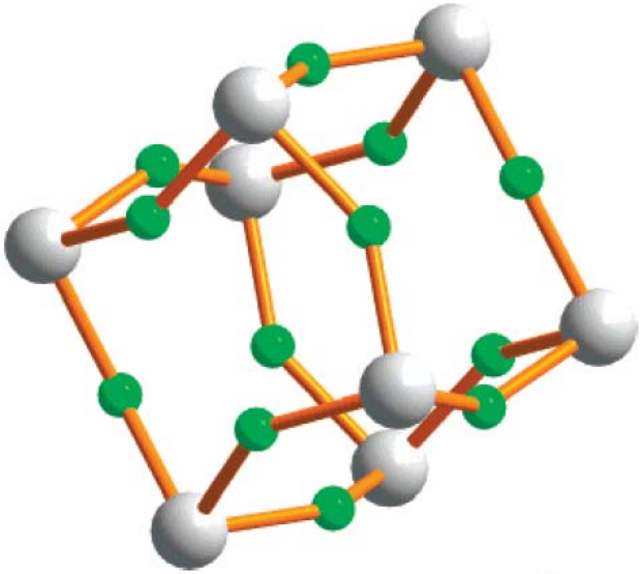
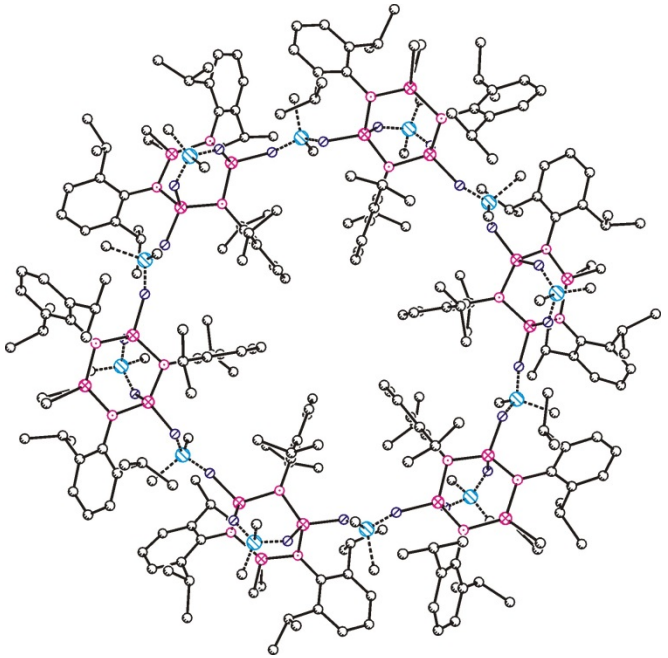
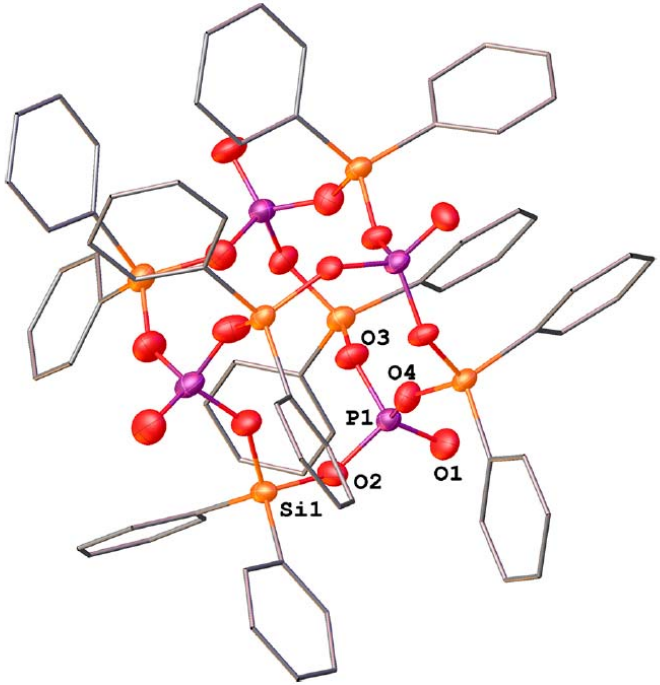
Rings and Polyhedra

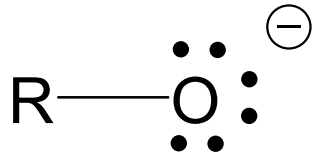






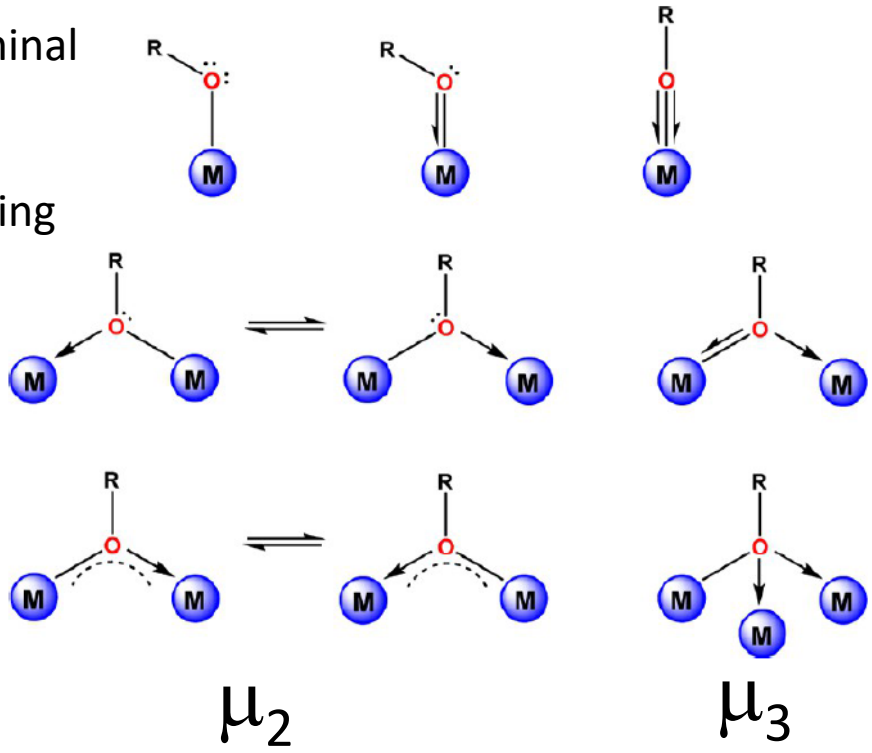
Alkoxide Coordination Modes

Metal alkoxides

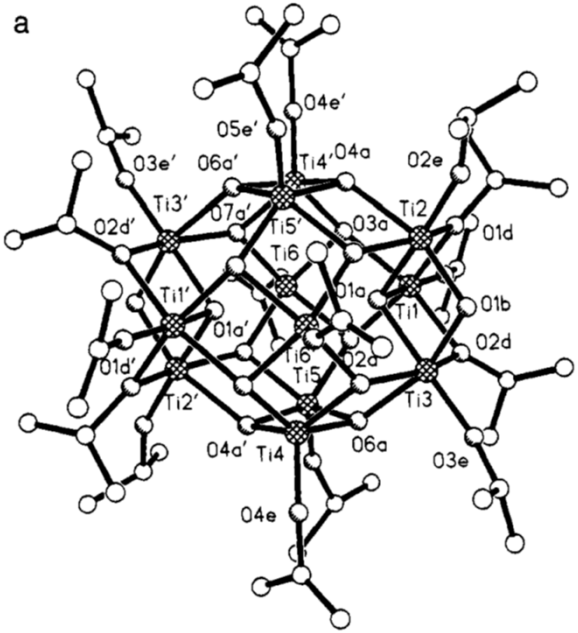


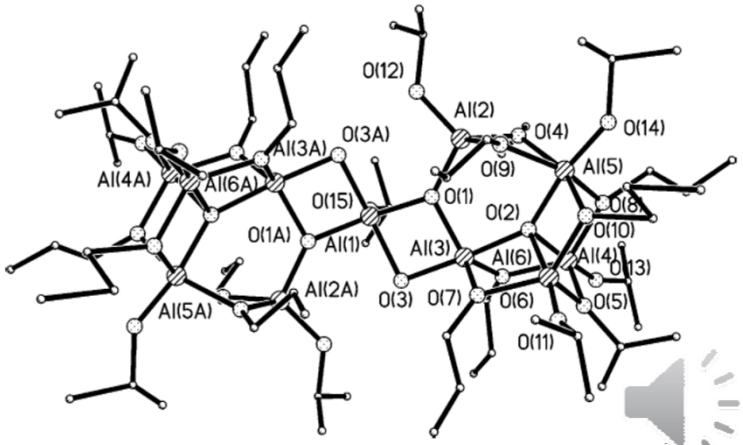
Terminal

Bridging



μ_2 μ_3





“Harris” Notation

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

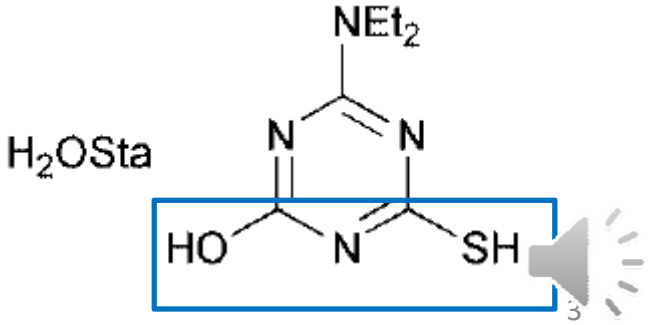
The binding mode is referred to as $[X.Y_1Y_2Y_3 \ldots Y_n]$

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

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

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**



“Harris” Notation

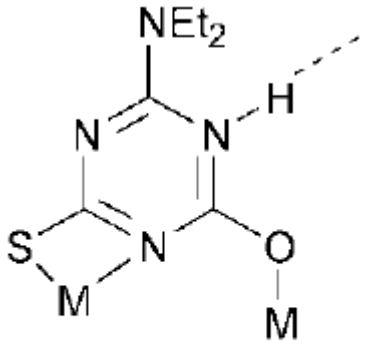
S > O > N

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

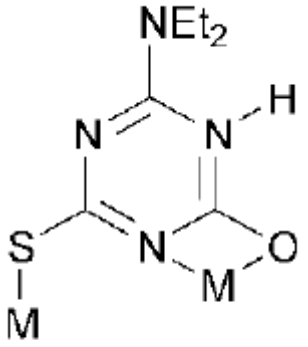
While the chelating N,S mode is inherently more likely (and observed), there is still a need to distinguish between this and the N,O-chelating mode
To distinguish between these two alternatives include a **subscript** number to show to which **metal atom** the donor is attached

The mode [$2.1_1 1_2 1_1$] implies the N- and S-donors chelate to one metal and the O atom binds to the second metal

The mode [$2.1_1 1_2 1_2$] implies the N- and O-donors chelate and the S-donor binds to the second metal



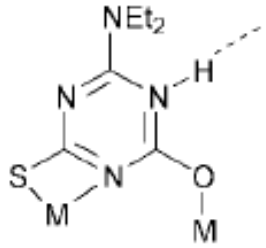
$2.1_1 1_2 1_1$



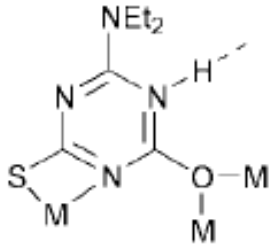
$2.1_1 1_2 1_2$

“Harris” Notation

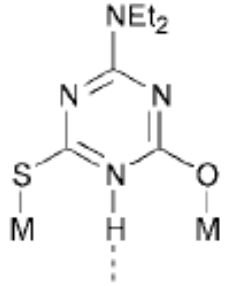
S > O > N



$2.1_1 1_2 1_1$



$3.1_1 2_{23} 1_1$



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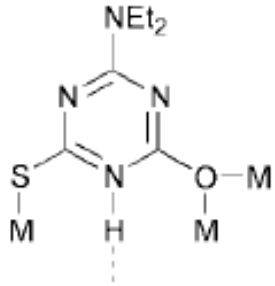

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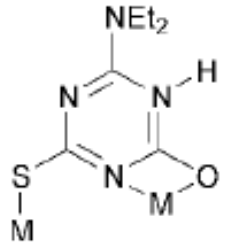


$2.1_1 1_2 1_2$

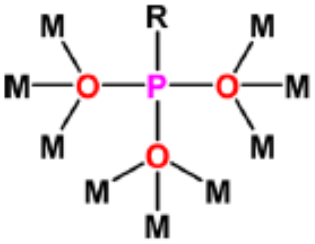
Five possible bonding modes for ligand $OStaH^-$

The numbers below each bonding mode refer to the Harris notation

The mode $[2.1_1 1_2 1_2]$ shows how Harris notation distinguishes between possible binding modes (*cf.* $[2.1_1 1_2 1_1]$).

The dashed lines to H atoms indicate hydrogen bonds

Coordination Modes of the Phosphonato Ligands



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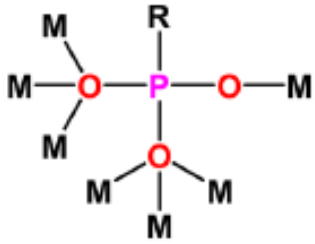

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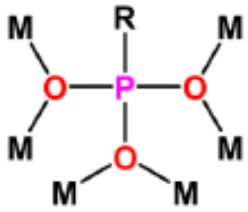
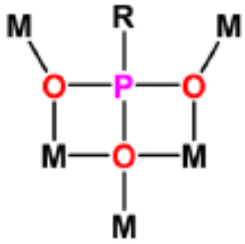


6.222



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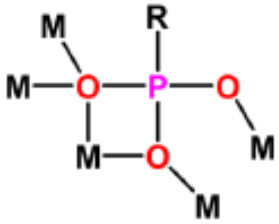

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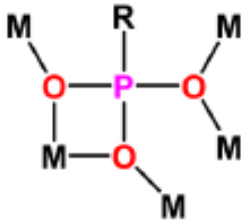

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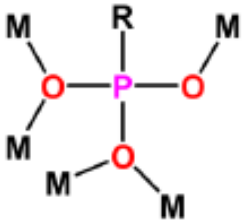

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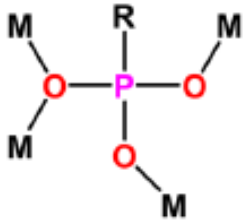
4.212



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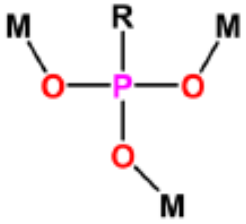
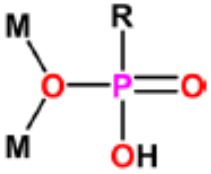


3.111

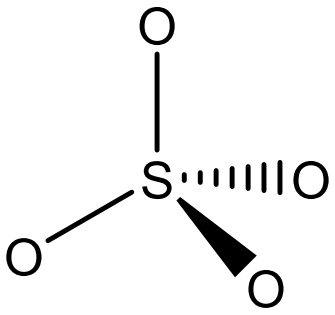
3.210

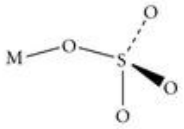
2.110



2.200

Crystallographically established coordination modes of the sulfato ligand





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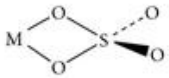

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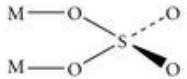

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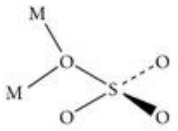

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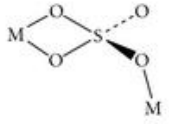
2.1111

2.2110



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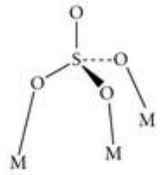

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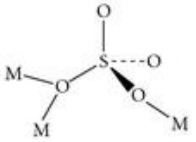

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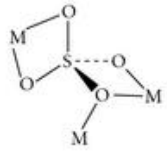

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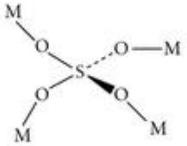

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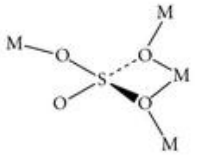

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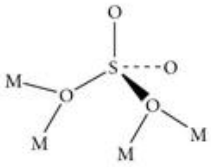

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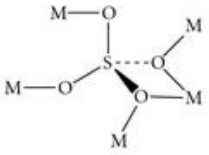

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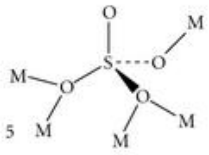

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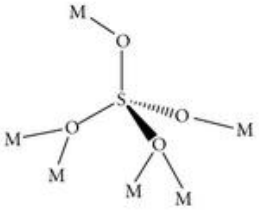

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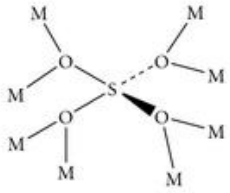

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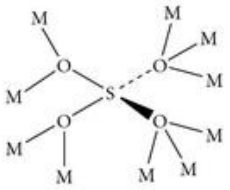
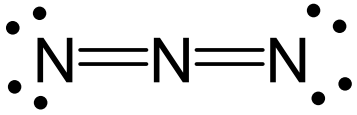
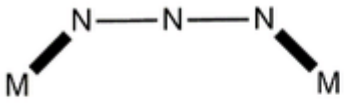


10.3322

“Harris” Notation

Crystallographically established bridging coordination modes of the azido ligand





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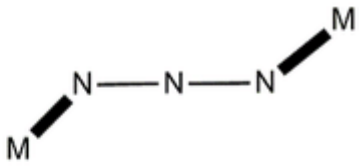
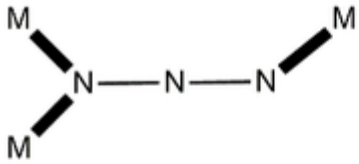


2.11/syn, anti



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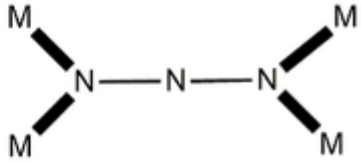

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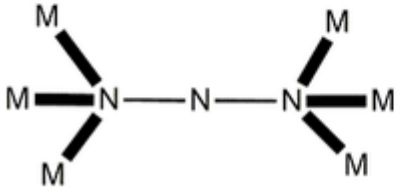

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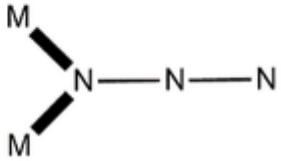

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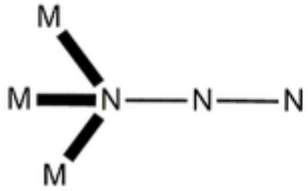

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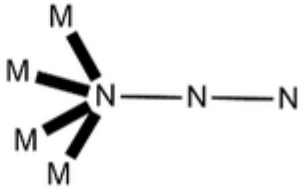


4.40

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

e_g

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

t_{2g}

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

$1a_{1g}$

Space Group Symbols

primitive (**P**), face-centered (**F**), body-centered (**I**), base-centered (**A**, **B**, **C**), rhombohedral (**R**)

S. G. Class	Centering	Symbol syntax (examples)
Triclinic	P	P1, P-1
Monoclinic	P, C, B	Paxis, Pplane, Paxis/plane (**$P2_1$, Cm**, **$P2_1/c$**)
Orthorhombic	P, F, I, C, A	Paxisaxisaxis, Pplaneplaneplane (**Pmmm, $Cmc2_1$**)
Tetragonal	P, I	P**4**, P4axisaxisaxis, P4planeplaneplane (**I4/m, P4mm**)
Trigonal	P, R	P**3**axis, P3plane (**R-3m**)
Hexagonal	P	P**6**, P6axisplane (**$P6_3/mmc$**)
Cubic	P, F, I	Paxis**3**plane, Pplane**3**plane (**Pm-3m, Fm-3m**)

m = plane of symmetry, **2** = two-fold, **3** = three-fold, **6** = six-fold axis, **-1** = inversion center

Strukturbericht Symbols

A partly systematic method for specifying the structure of a crystal
A - monatomic (elements), **B** - diatomic with equal numbers of atoms of each type (AB),
C - a 2-1 abundance ratio (AB_2), **D**0 - 3-1, etc.

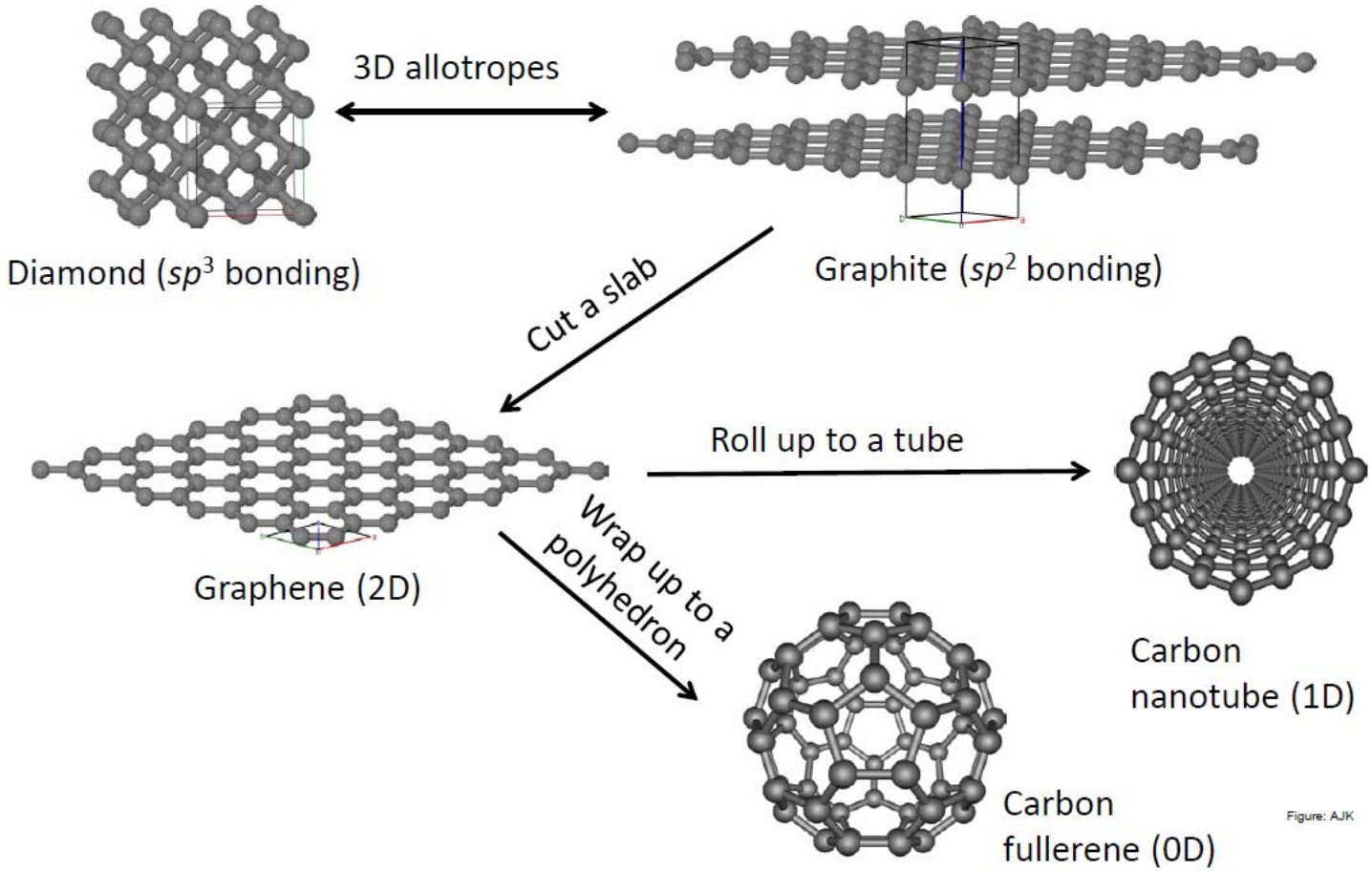
Structure Type	Struktur bericht	Space Group (S.G. No.)	Lattice
Cu	**A1**	Fm-3m (225)	fcc
W, Fe	**A2**	Im-3m (229)	bcc
Mg	**A3**	$P6_3/mmc$ (194)	hcp
C - diamond	**A4**	Fd-3m (227)	Diamond
NaCl	**B1**	Fm-3m (225)	Rock salt
CsCl	**B2**	Pm-3m (221)	
ZnS	**B3**	F43m (216)	Zincblende
ZnS	**B4**	$P6_3/mc$ (186)	Wurtzite
CaF_2	**C1**	Fm-3m (225)	Fluorite

Pearson Symbols

Indicate the crystal symmetry and the number of atoms in the unit cell
e.g.: NaCl - a face-centered (**F**) cubic (**c**) structure with 8 atoms in the unit cell = cF8
monoclinic (**m**), hexagonal (**h**), orthorhombic (**o**), asymmetric (**a**), primitive (**P**)
the Pearson symbol does not necessarily specify a unique structure (see cF8)

Structure Type	Pearson Symbol	Struktur bericht	Space Group (S.G. No.)
Cu	**cF4**	**A1**	Fm-3m (225)
W, Fe	**cI2**	**A2**	Im-3m (229)
Mg	**hP2**	**A3**	$P6_3/mmc$ (194)
C - diamond	**cF8**	**A4**	Fd-3m (227)
NaCl	**cF8**	**B1**	Fm-3m (225)
CsCl	**cP2**	**B2**	Pm-3m (221)
ZnS (zb)	**cF8**	**B3**	F43m (216)
ZnS (w)	**hP4**	**B4**	$P6_3/mc$ (186)
CaF_2	**cF12**	**C1**	Fm-3m (225)

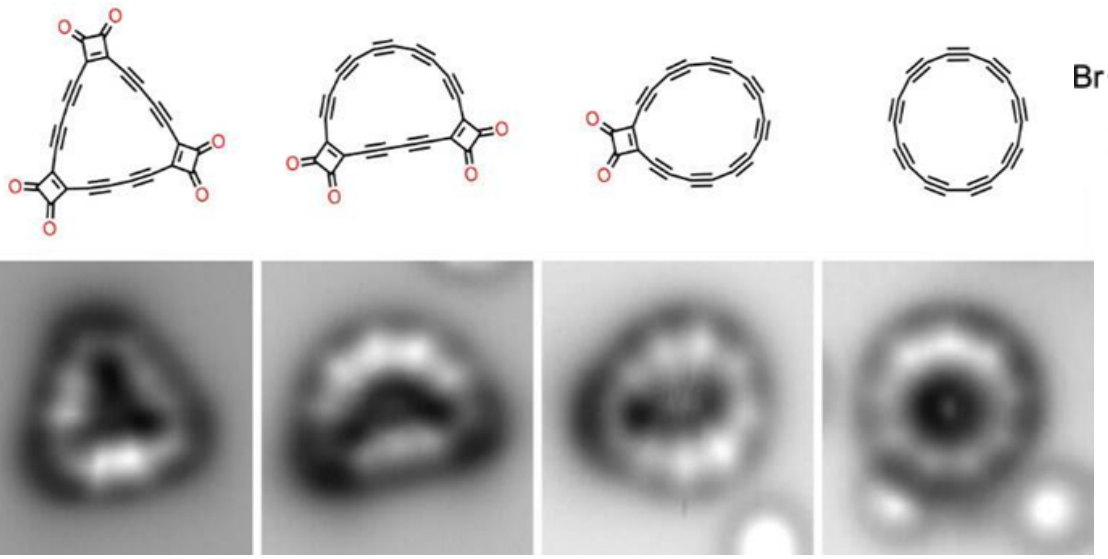
Allotropes of Carbon



C_{18} Allotrope of Carbon

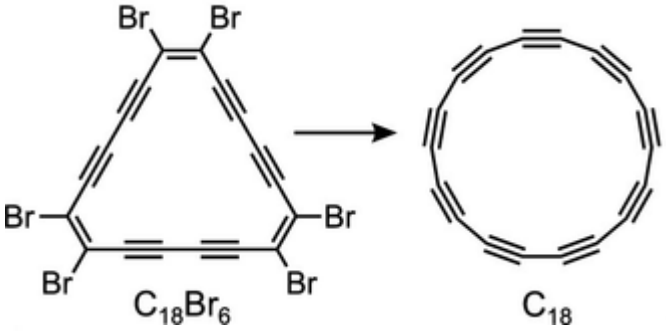
On-surface formation of C_{18} on bilayer NaCl on Cu(111) at 5 K, p ≈ 10^{-11} mbar, via voltage pulses >1.2 V in STM/AFM

Decarbonylation

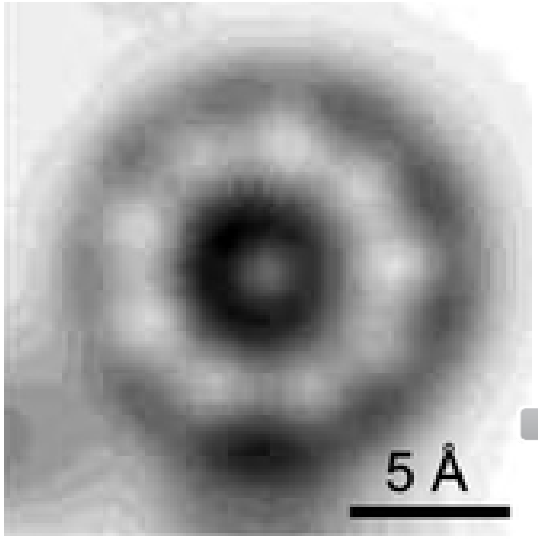


13% yield

Debromination



21 single molecule reactions
64% yield

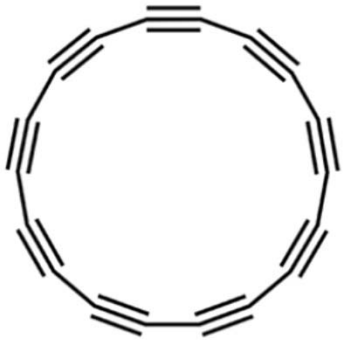


Science **2019**, 10.1126/science.aay1914
JACS **2020** *142* (30), 12921, 10.1021/jacs.0c05033

C_{18} Allotrope of Carbon

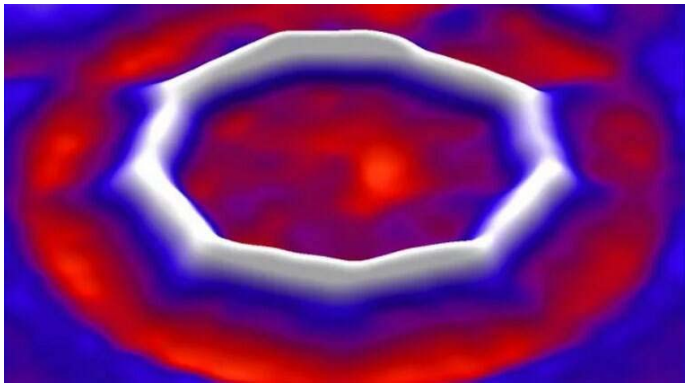
High-resolution atomic force microscopy
C_{18} - polyynic structure of carbon atoms with an alternating triple and single bonds

Semiconductor



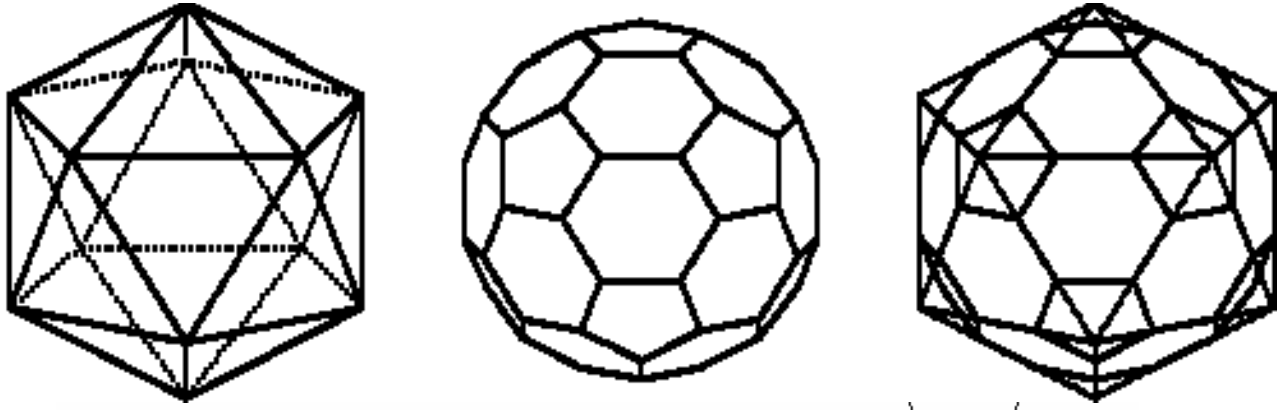
polyynic
D_{9h}, BLA ≠ 0

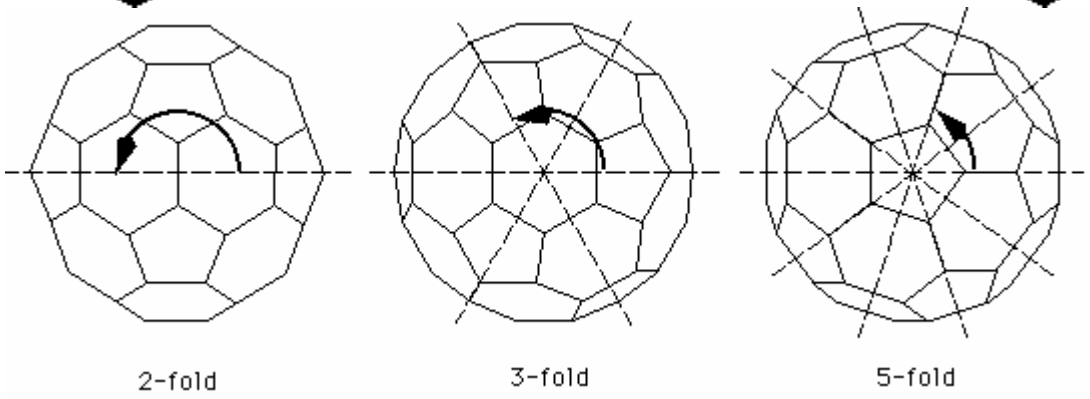
cumulenic
D_{18h}, BLA = 0

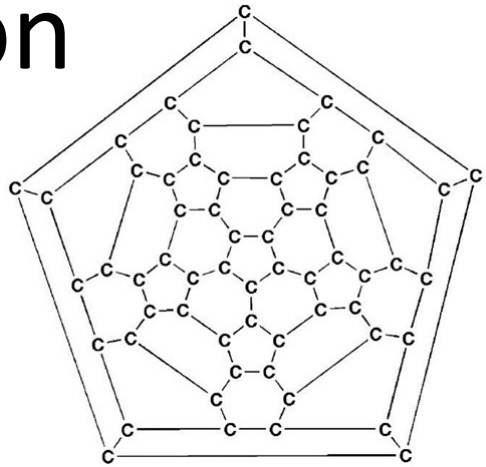


Allotropes of Carbon

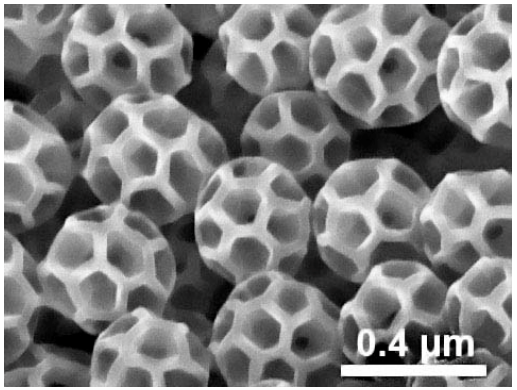
Fullerene C_{60}







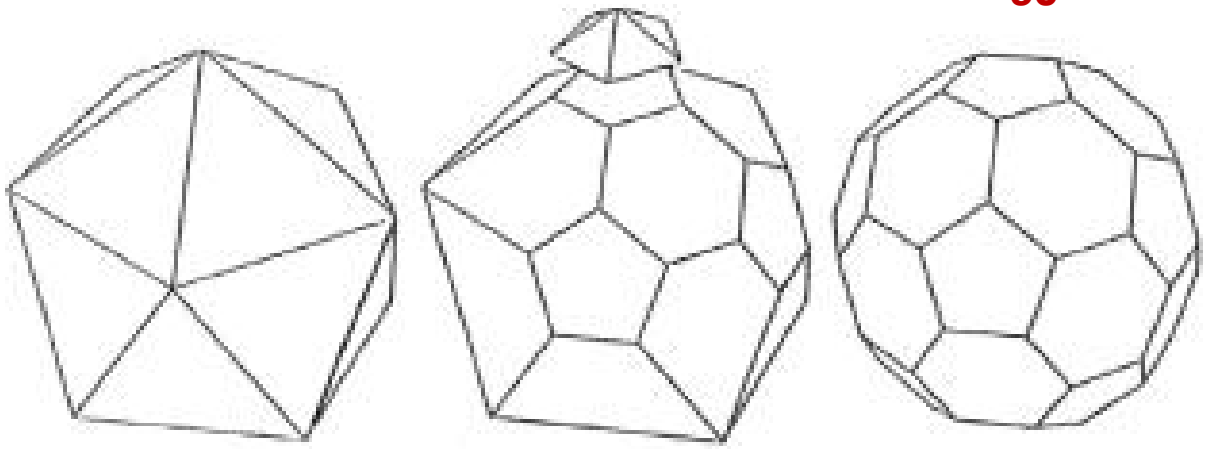
Schlegel diagram



Brochosomes of leafhoppers

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

C_{60} Fullerene

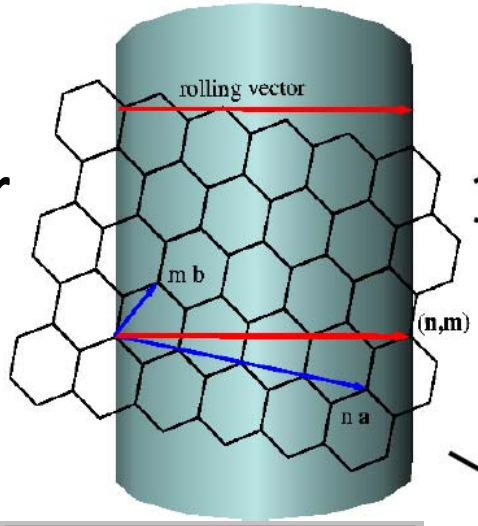


Icosahedron

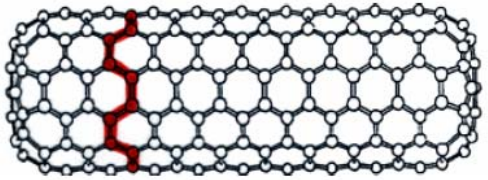
Truncated icosahedron

(n,m) SWNTs

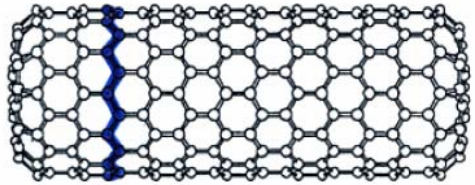
Chiral vector (n,m)



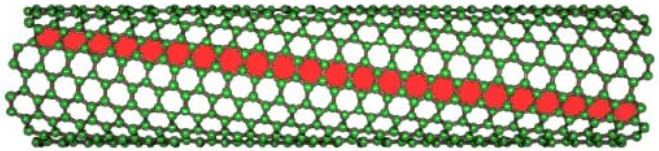
(n,n) armchair

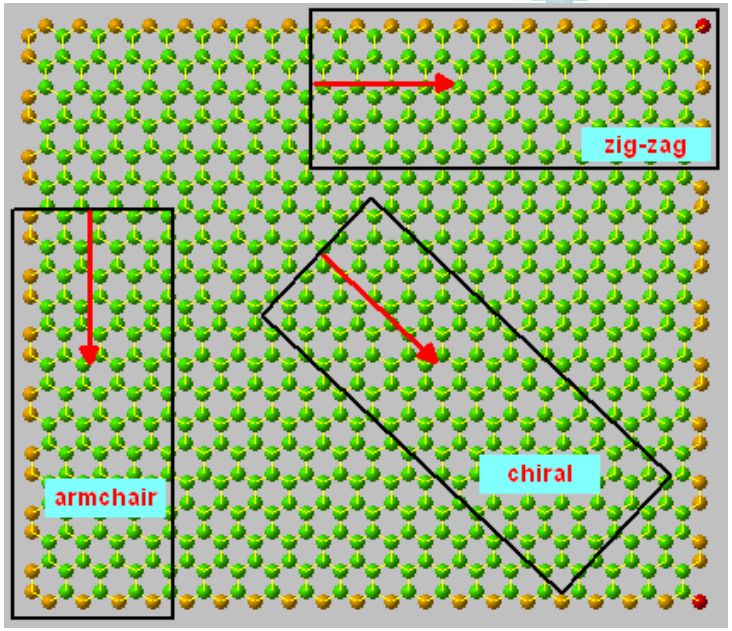


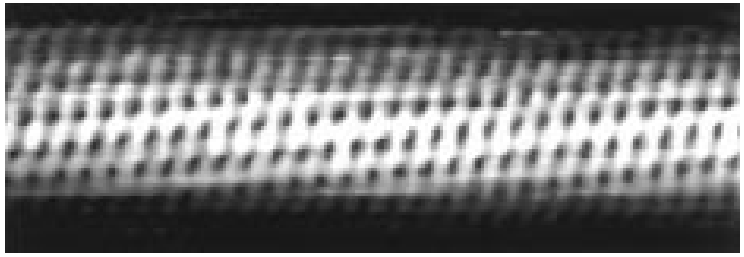
(n,0) zigzag



(n,m) chiral

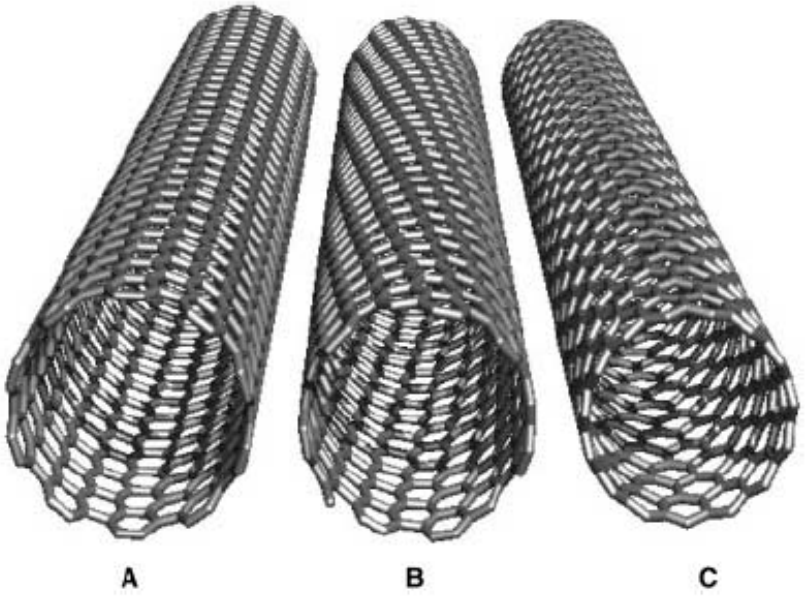


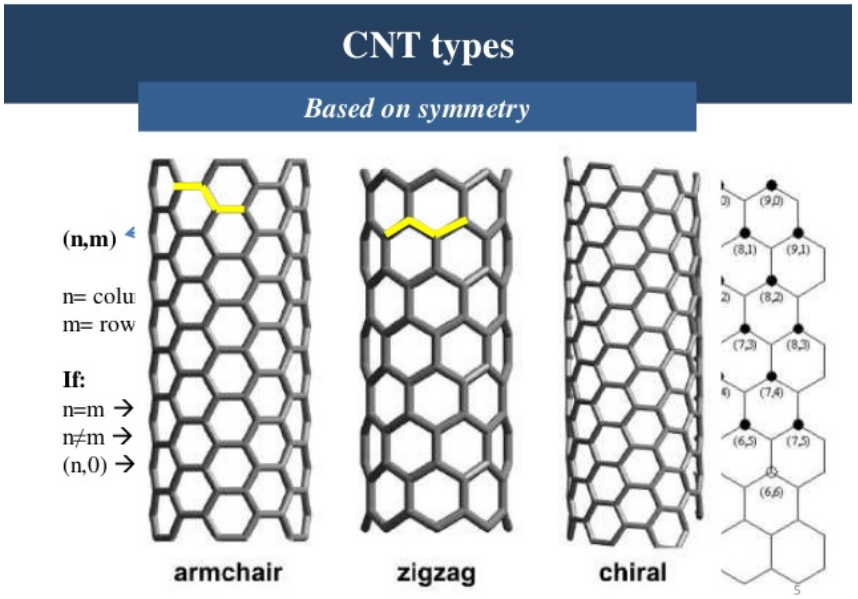




TEM of a chiral CNT

(n,m) SWNTs

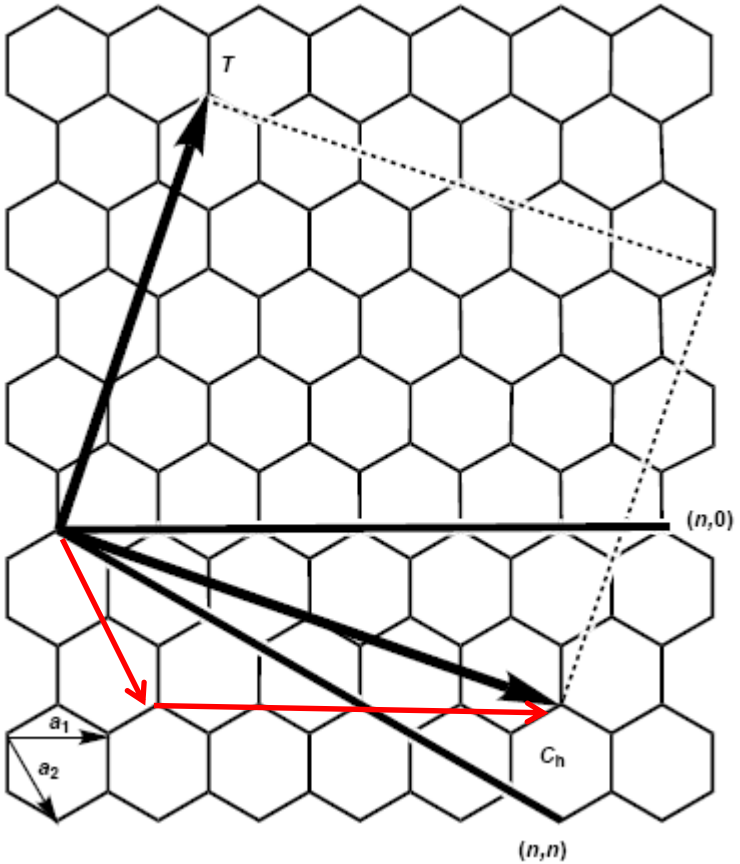




A) Armchair - an achiral metallic conducting (10,10) tube
B) Chiral - semiconducting (12,7) tube
C) Zigzag - an achiral conducting (15,0) tube

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 $C_h = n a_1 + m a_2$

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

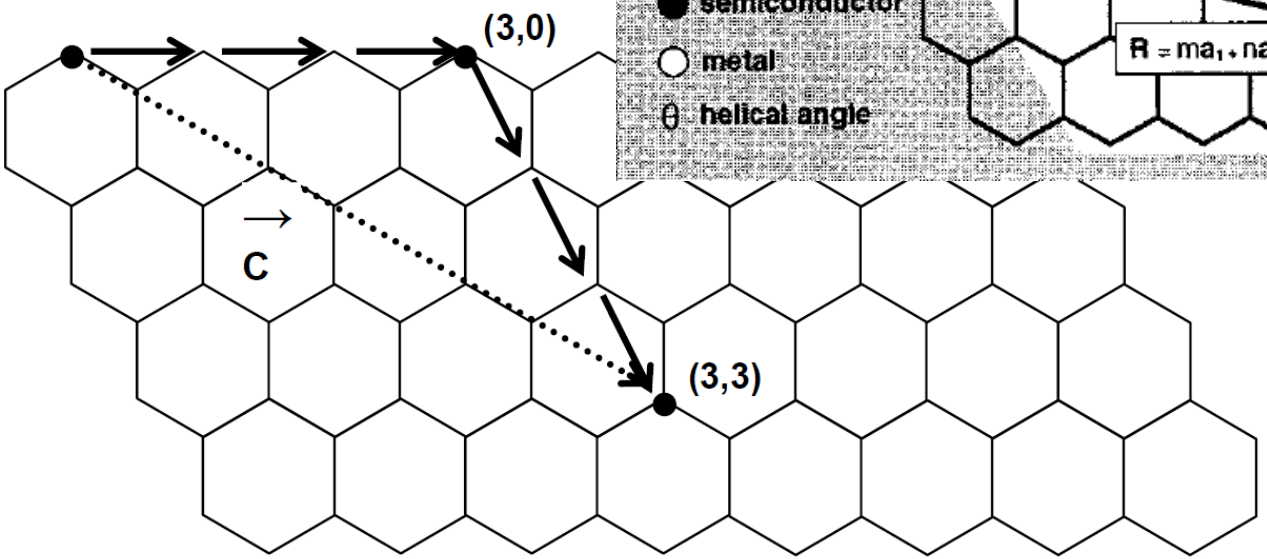
The rectangle represents an unrolled unit cell, defined by T and C_h

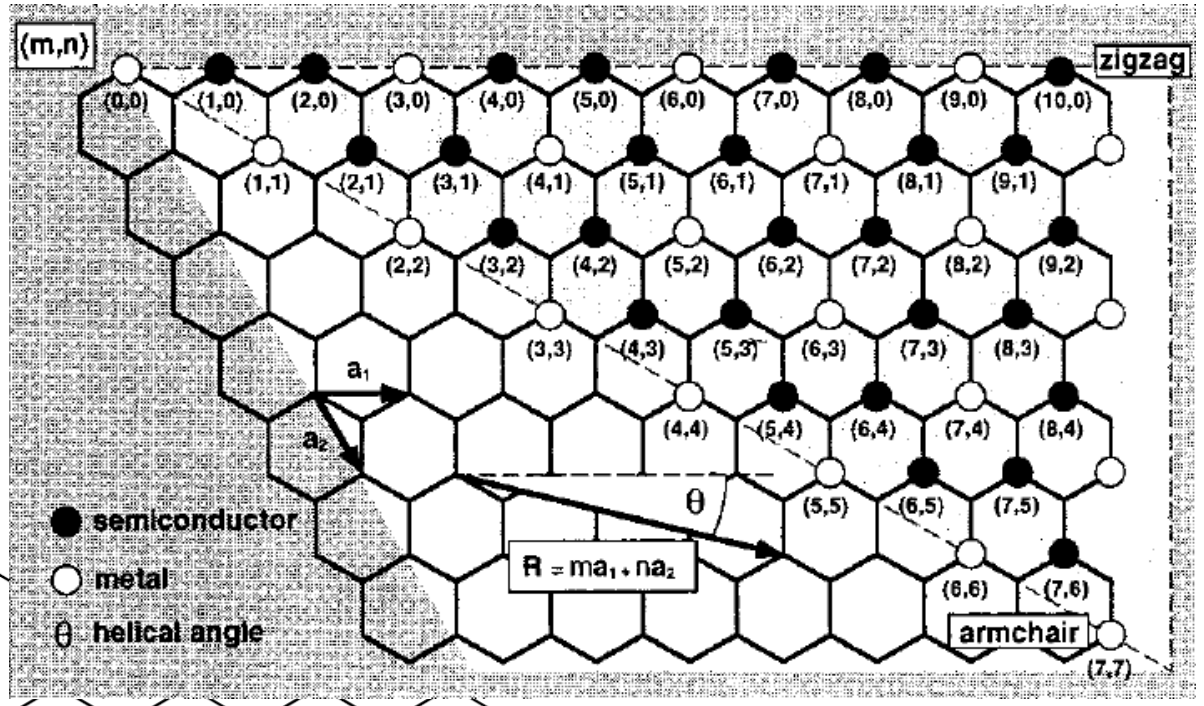
Roll-up of (n,m) SWNTs

Chiral vector:

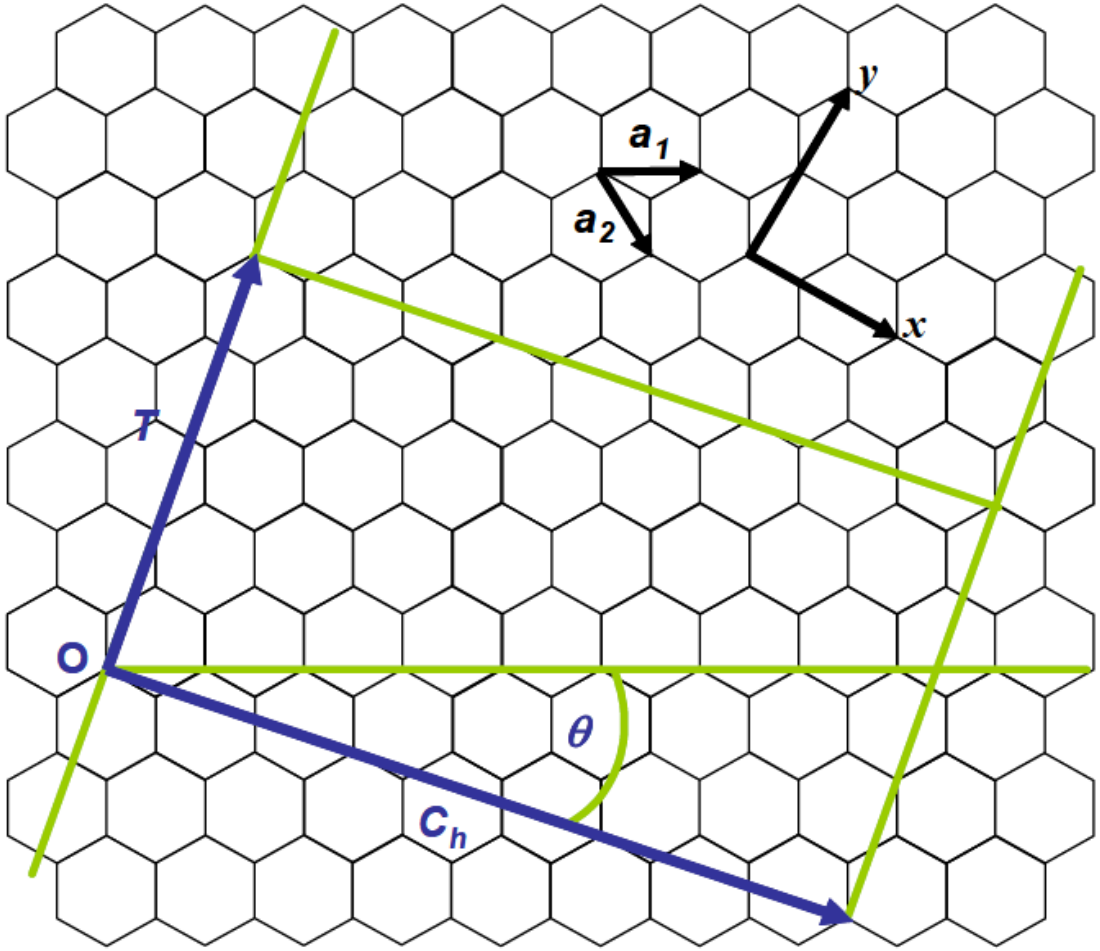
$C_h = na_1 + ma_2$

(n,m) = (3,3)





Roll-up of (n,m) SWNTs



d(Csp^2-Csp^2) = 1.42 Å

$a_0 = a_1 = a_2$

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

Roll-up of (n,m) SWNTs

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

Tube diameter

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

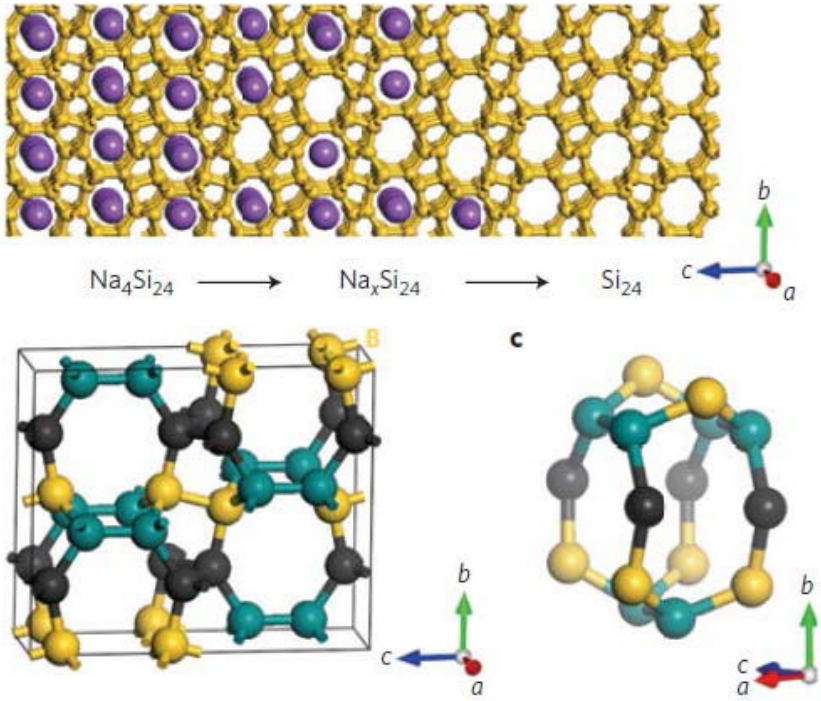
$$|a_1| = |a_2| = a_0 = 0.249 \text{ nm}$$

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

θ = 0 - 30°

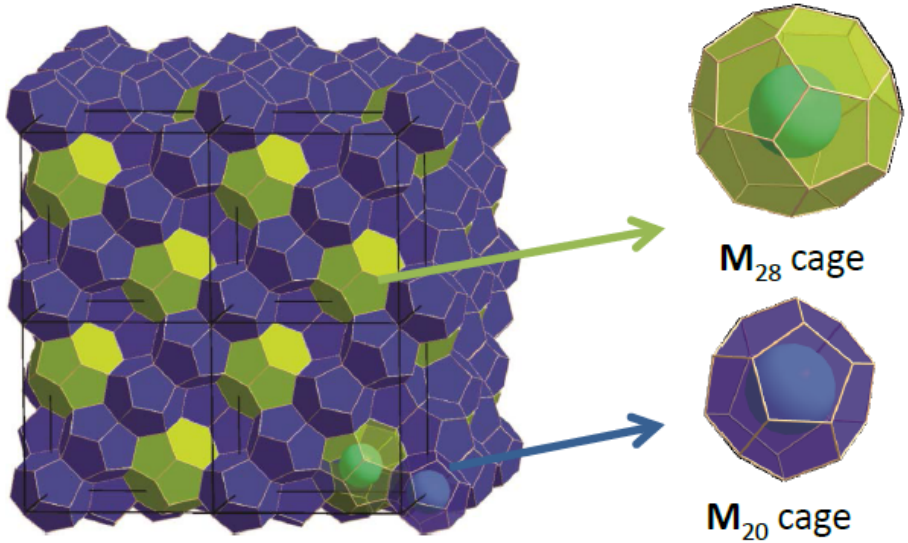
Allotropes of Silicon

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



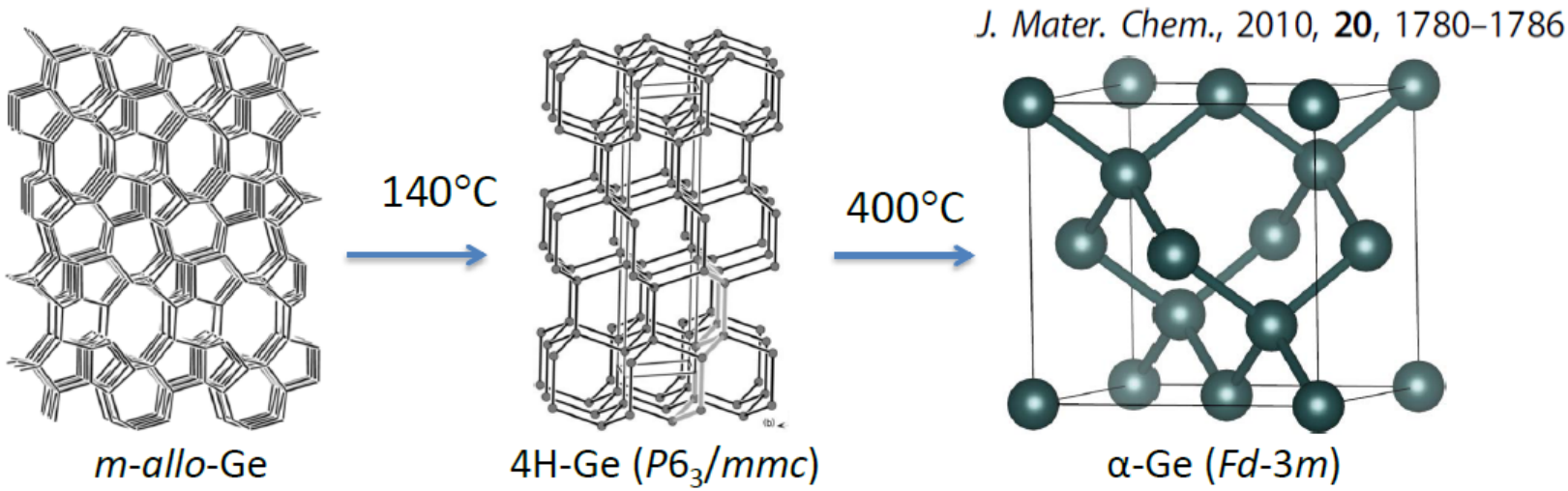
Si_{136} and Ge_{136} Clathrate II Fd-3m

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



Allotropes of Germanium

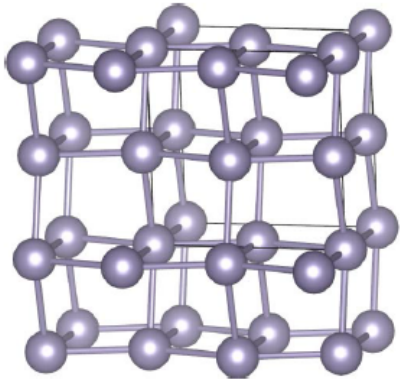
120 kilobars, allotrope *beta*-germanium = white-tin
2014 - the vapor of germanium deposited on a gold surface
by molecular beam epitaxy, a 2D single-layered “germanene”

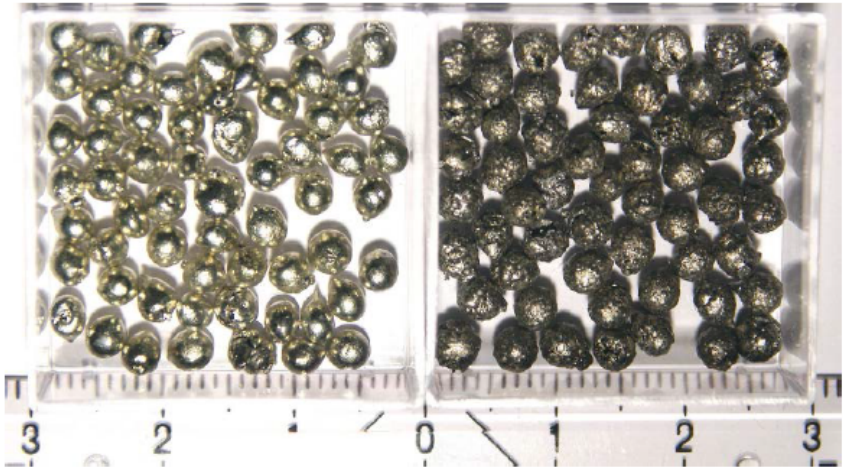


Expands as it solidifies
Semiconductor, refined to impurity concentration of only 1 part in 10^{10}

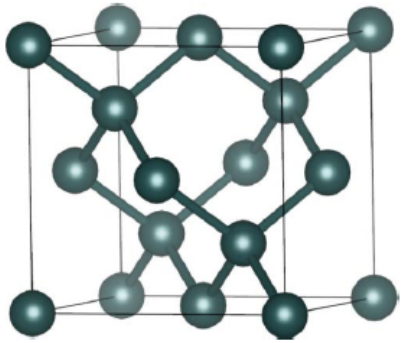
Allotropes of Tin

β-Sn ($I4_1/amd$)
white tin

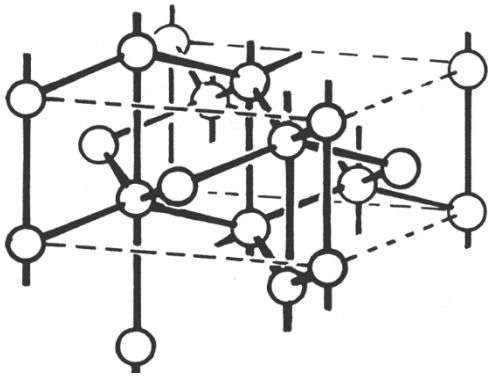


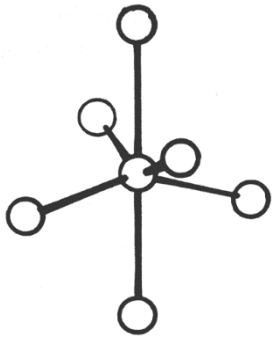


α-Sn (Fd-3m)
grey tin



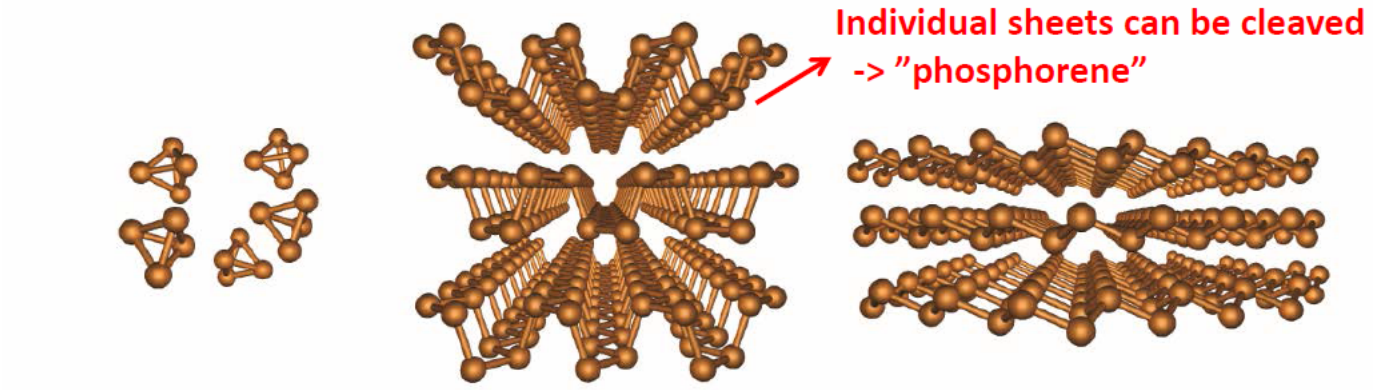
Beta White Sn (metallic)
Coordination number 6
Sn-Sn bond lengths 302 and 318 pm
a = 5.8319 Å, c = 3.1815 Å





Alpha Gray Sn - diamond type
stable below 13 °C, semiconductor
Coordination number 4
Sn-Sn bond length 281 pm
a = 6.4892 Å

Allotropes of Gr15 Elements

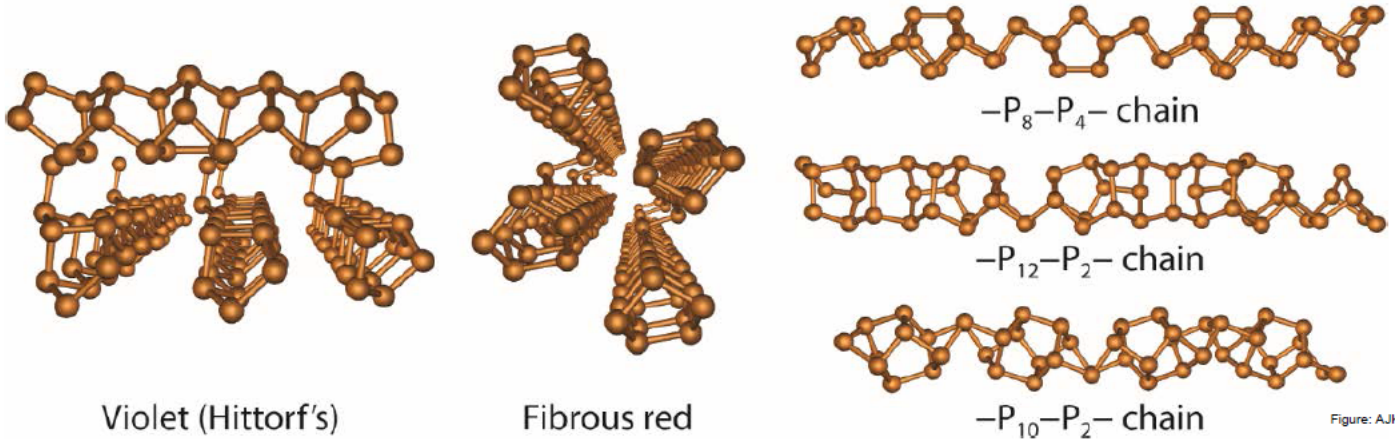


Tetrahedral molecules (P, As, Sb)

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)

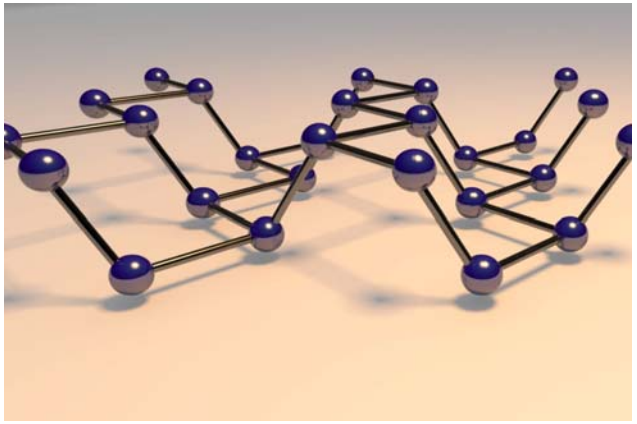
Fibrous red

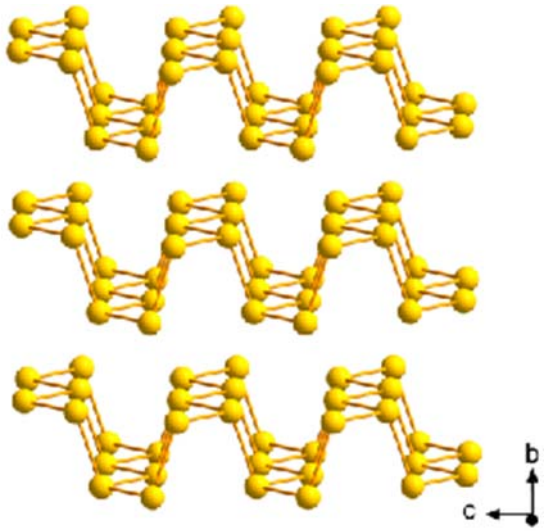
Figure: AJK

11

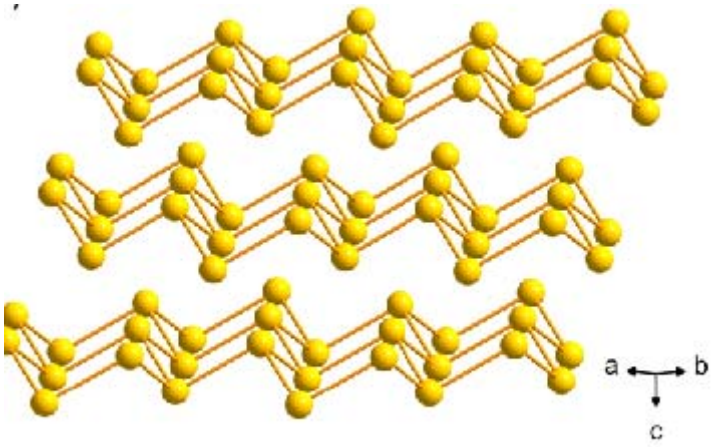
Allotropes of Gr15 Elements

Black phosphorus (orthorhombic)

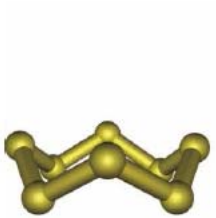




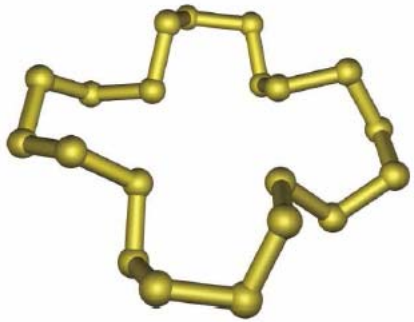
Gray arsenic (rhombohedral)



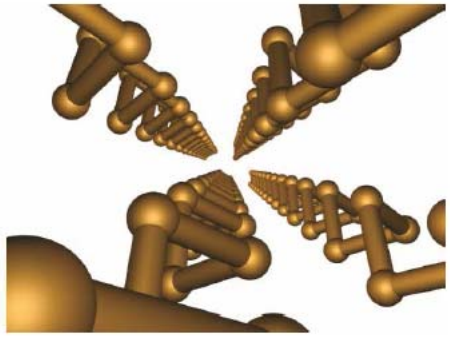
Allotropes of Gr16 Elements



α-orthorhombic cyclo-S_8



cyclo-S_{20}

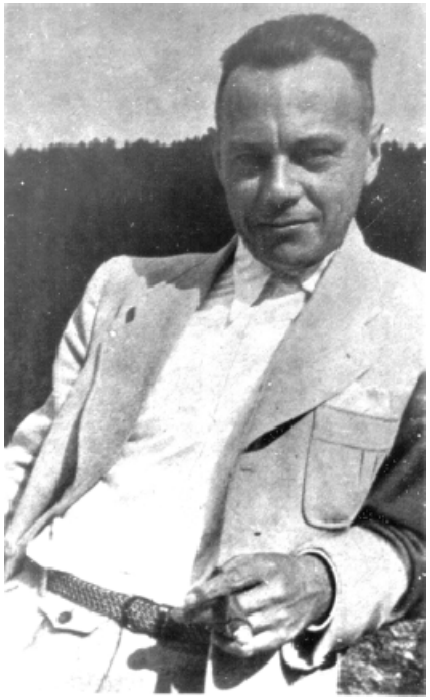


gray selenium and tellurium helical chains

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

1930's

Zintl Phases



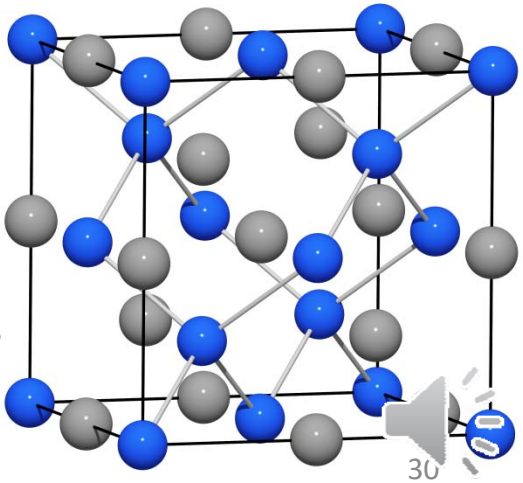
Eduard Zintl
(1898 – 1941)

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 can exhibit metallicity, ionicity, and covalency simultaneously

***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

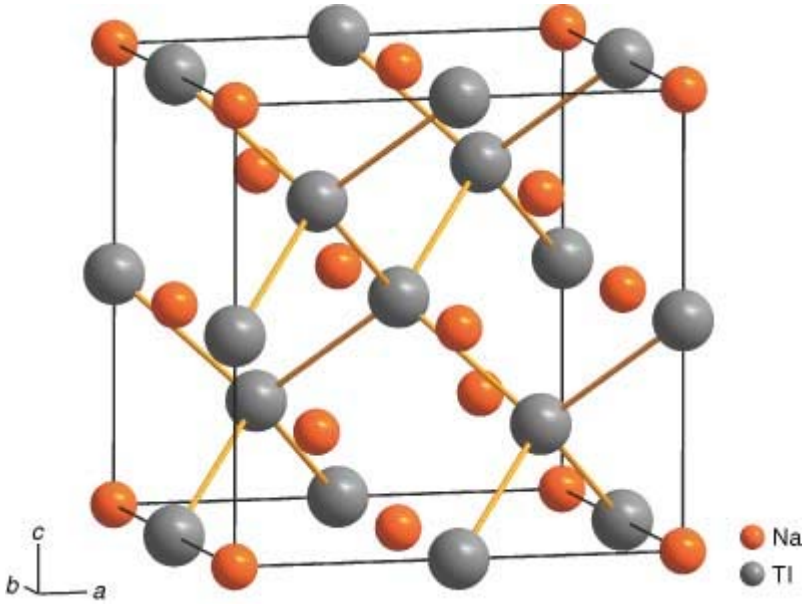
$$Ca + Si \rightarrow CaSi$$

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

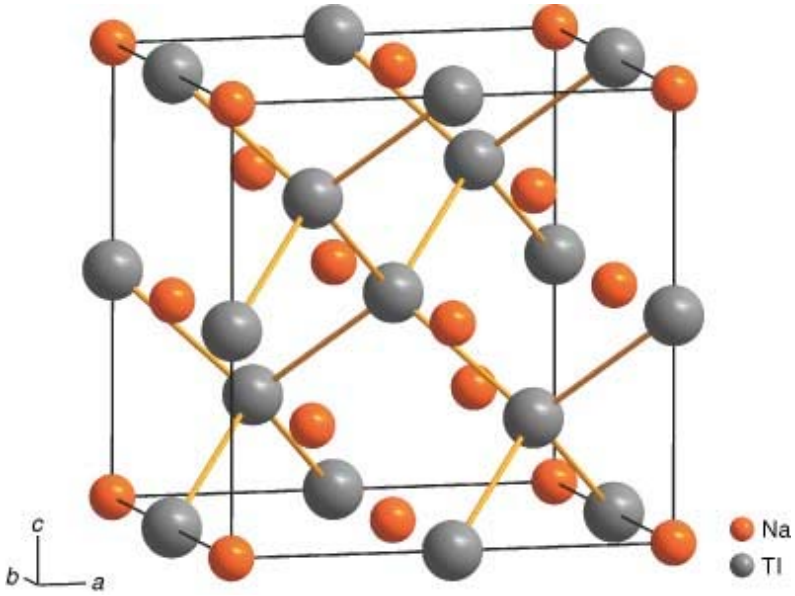
Zintl-Klemm Phases

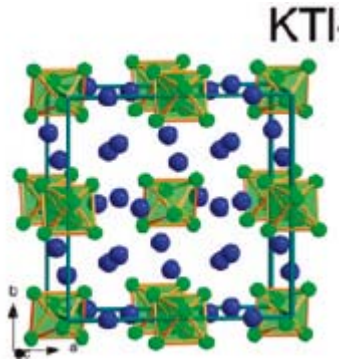
Wilhelm Klemm expanded the concept to the “pseudoatom” approach:
polyanions look like a following element

NaTl is the prototype Zintl phase - 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 Na/Tl 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)

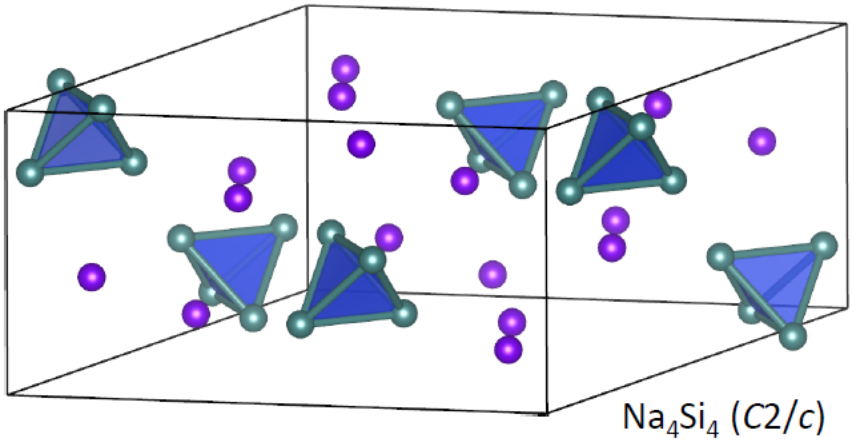
LiAl, LiGa, and LiIn form NaTl structure, KTl and contains Tl_6 distorted octahedra while LiTl adopts a CsCl-type structure

Zintl-Klemm Phases

NaSi (Na_4Si_4)

Each Na atom donates 1*e*–
Each Si atom accepts 1*e*–

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



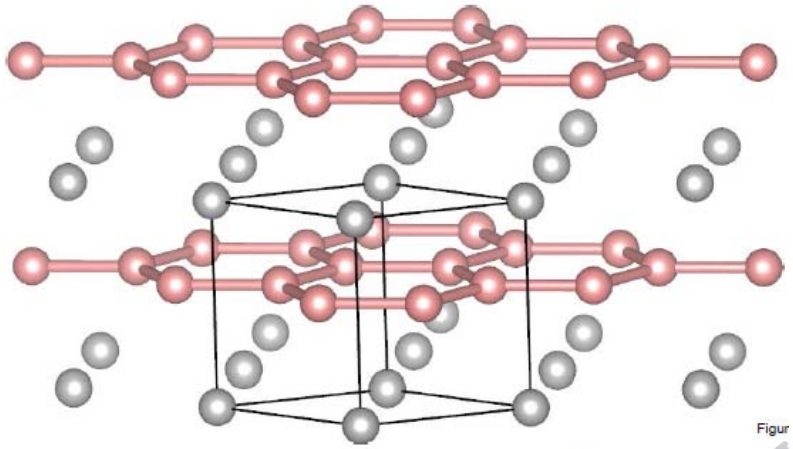
Na_4Si_4 (*C*2/*c*)

MgB_2

Each Mg atom donates 2*e*–
Each B atom accepts 1*e*–

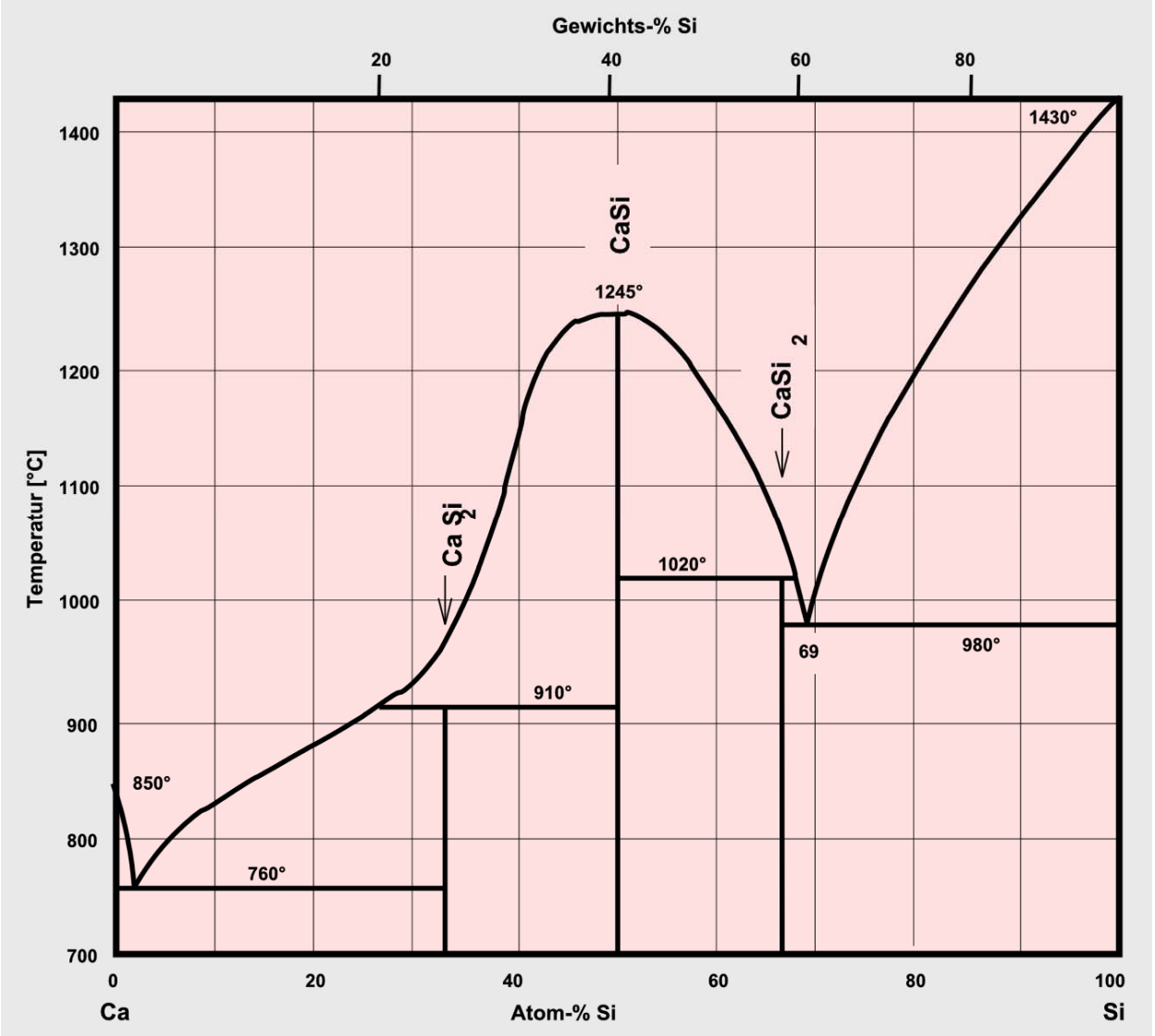
Two-dimensional B network isoelectronic with graphene, superconducting at T_c = 39 K

Sigma-bonding electrons are much more strongly superconducting than the pi-bonding ones



MgB_2 (*P*6/*mmm*)

Zintl-Klemm Phases

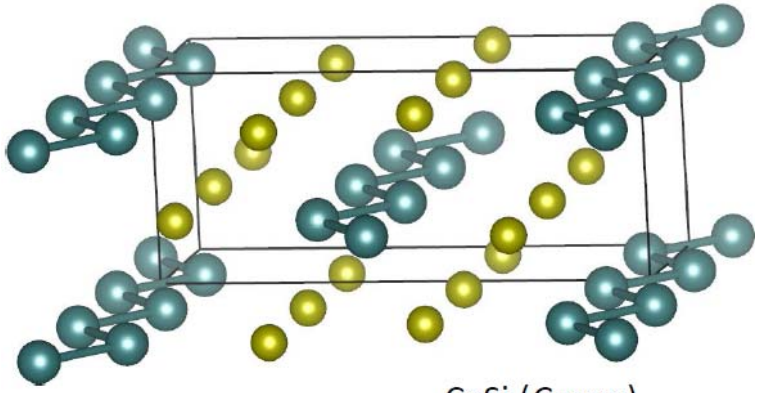


Zintl-Klemm Phases

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)

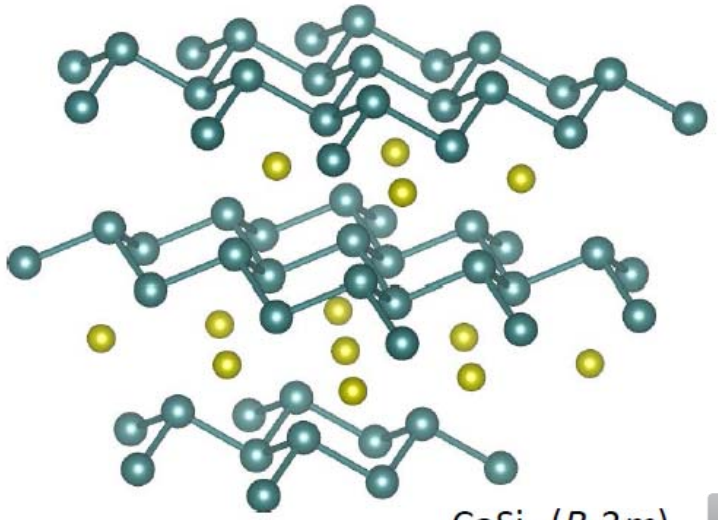


CaSi (*Cmcm*)

$CaSi_2$

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



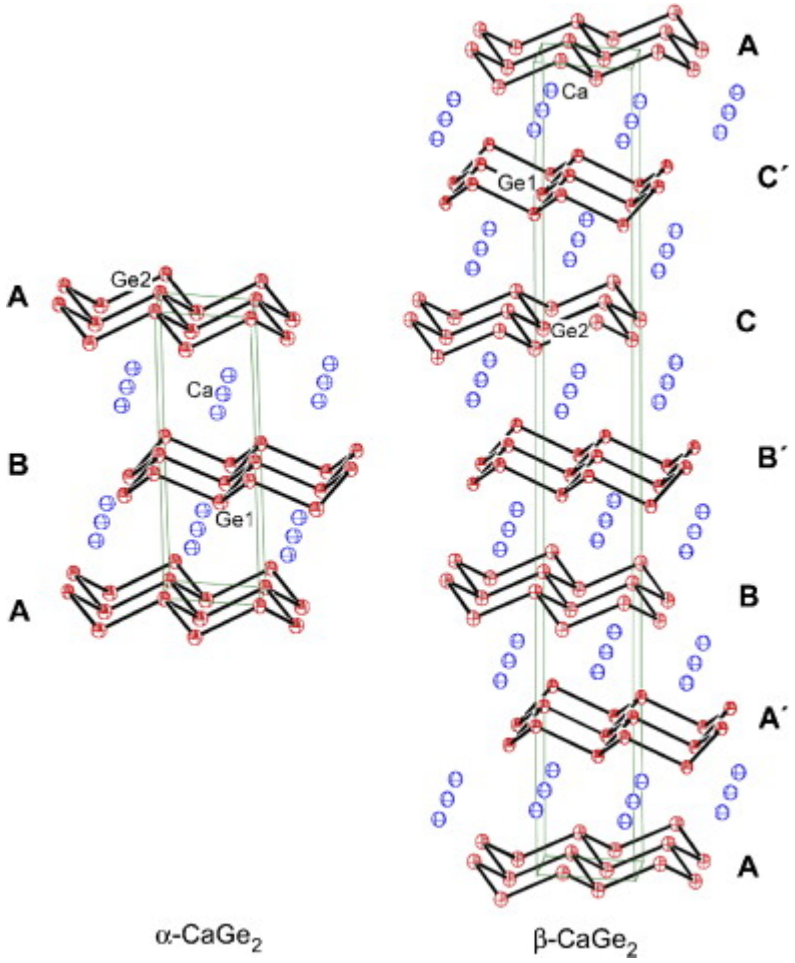
$CaSi_2$ (*R*-3*m*)

Zintl-Klemm Phases

$CaGe_2$

Each Ca atom donates $2e^-$
Each Ge atom accepts $1e^-$

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

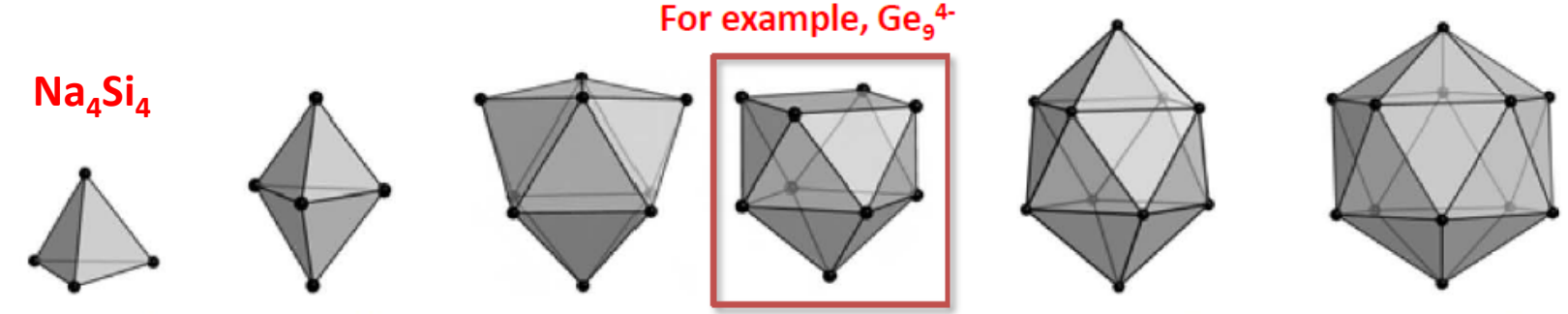


$CaGe_2 + 2\ HF \rightarrow CaF_2 + 2\ GeH$

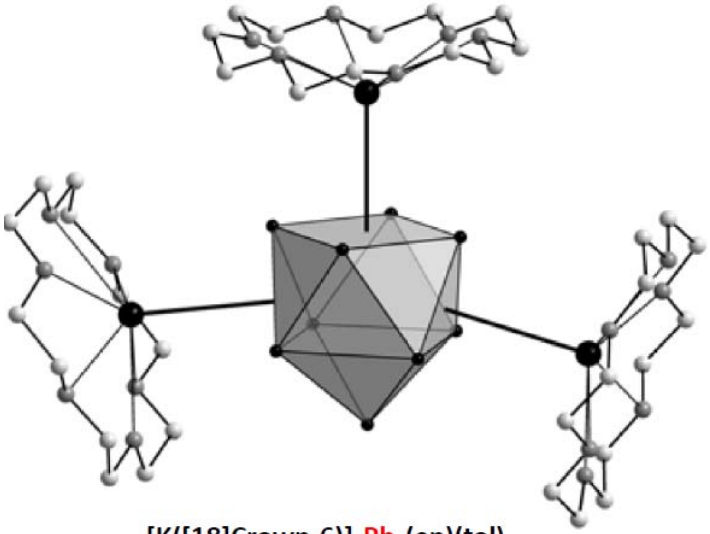
Zintl-Klemm Phases

Na_4Si_4

For example, Ge_9^{4-}

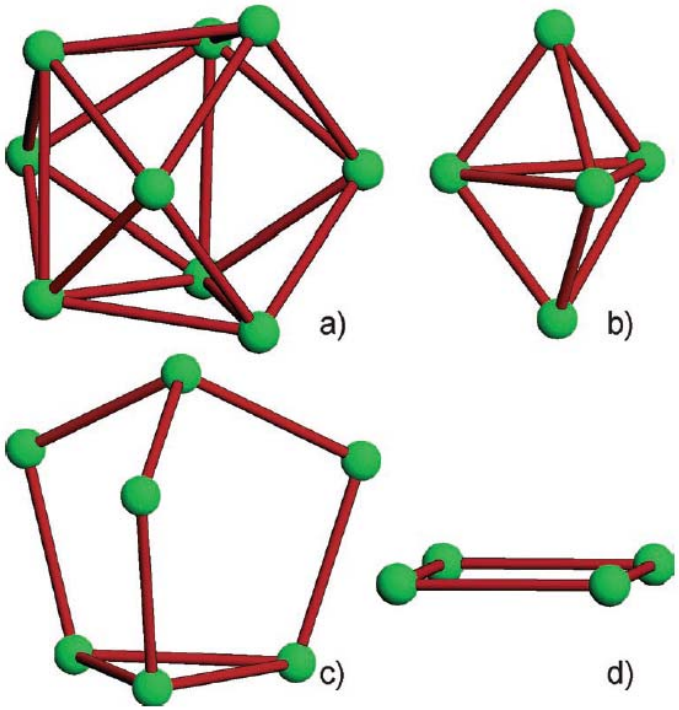


(a) $[E_4]^{4-}$ (b) $[E_5]^{2-}$ (c) $[E_9]^{x-}$ (d) $[Pb_{10}]^{2-}$ (e) $[E_{12}]^{2-}$



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

Deltahedral Zintl Ions



The main-group anionic clusters
Crystallized from solutions with
sequestered alkali-metal cations (crowns)

(a) Si_9^{2-}, E_9^{3-} and E_9^{4-} for E = Ge, Sn, Pb

E_9^{4-} = nido clusters, $2n + 4 = 22$

(b) E_5^{2-} for E = Ge, Sn, Pb

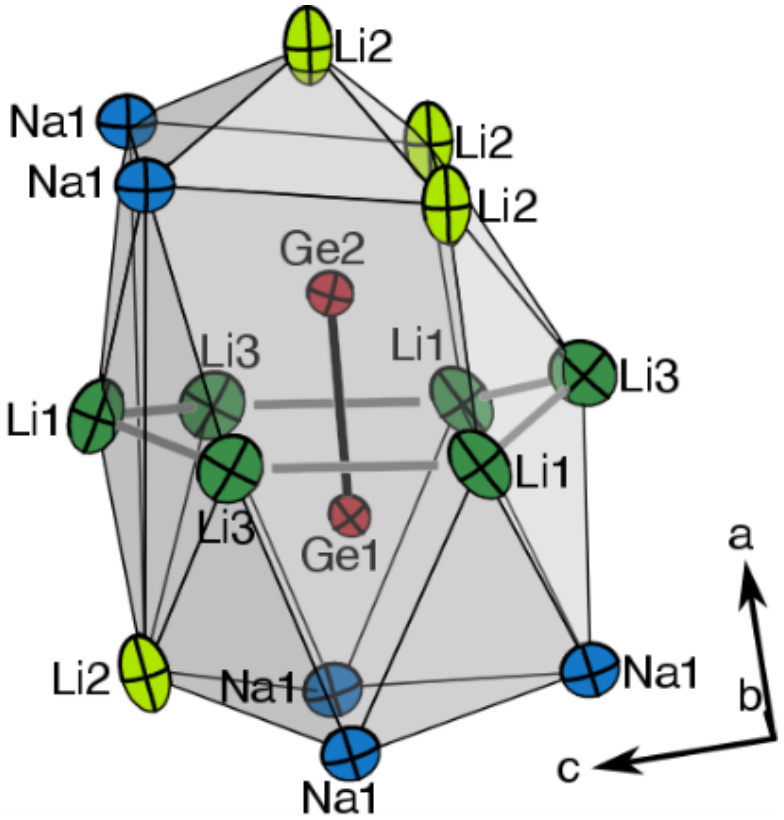
(c) As_7^{3-} and Sb_7^{3-}

(d) Sb_4^{2-} and Bi_4^{2-}

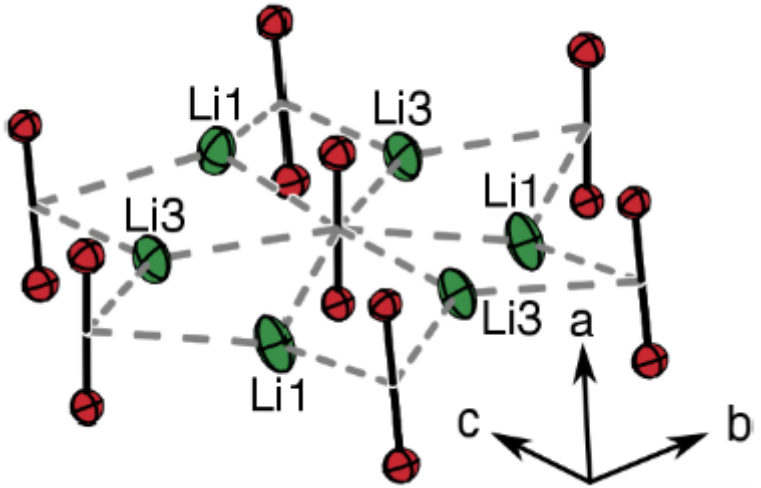
E_9^{4-} = monocapped square antiprism
or
distorted tricapped trigonal prisms

Ge, Sn, Pb - the three differently charged clusters E_9^{2-}, E_9^{3-} and E_9^{4-} coexist in solution in complex equilibria with solvated electrons

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



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



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

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

Each Ge atom accepts $2e^-$

Bond distance Ge=Ge

Raman spectroscopy – Ge=Ge stretching

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

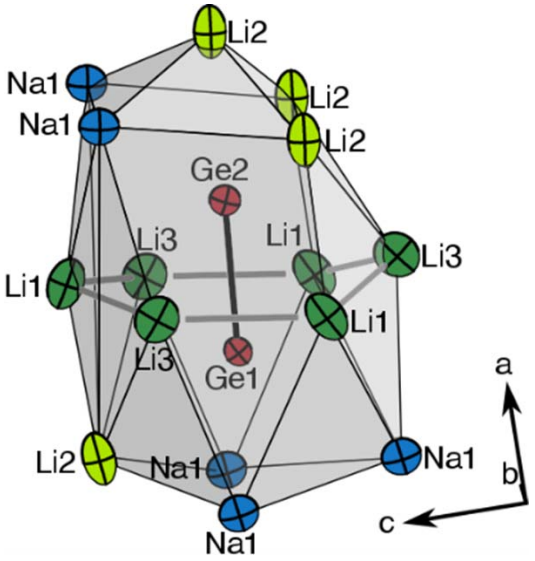
MO calculation

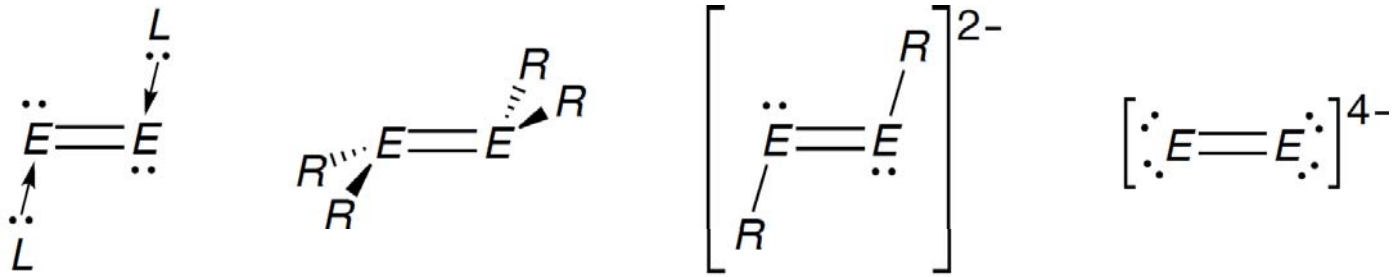
Band structure calculation

Bond Lengths in E=E (Si and Ge)

$[Ge_2]^{4-}$ bond distance in Li_3NaGe_2 **2.390(1) Å**

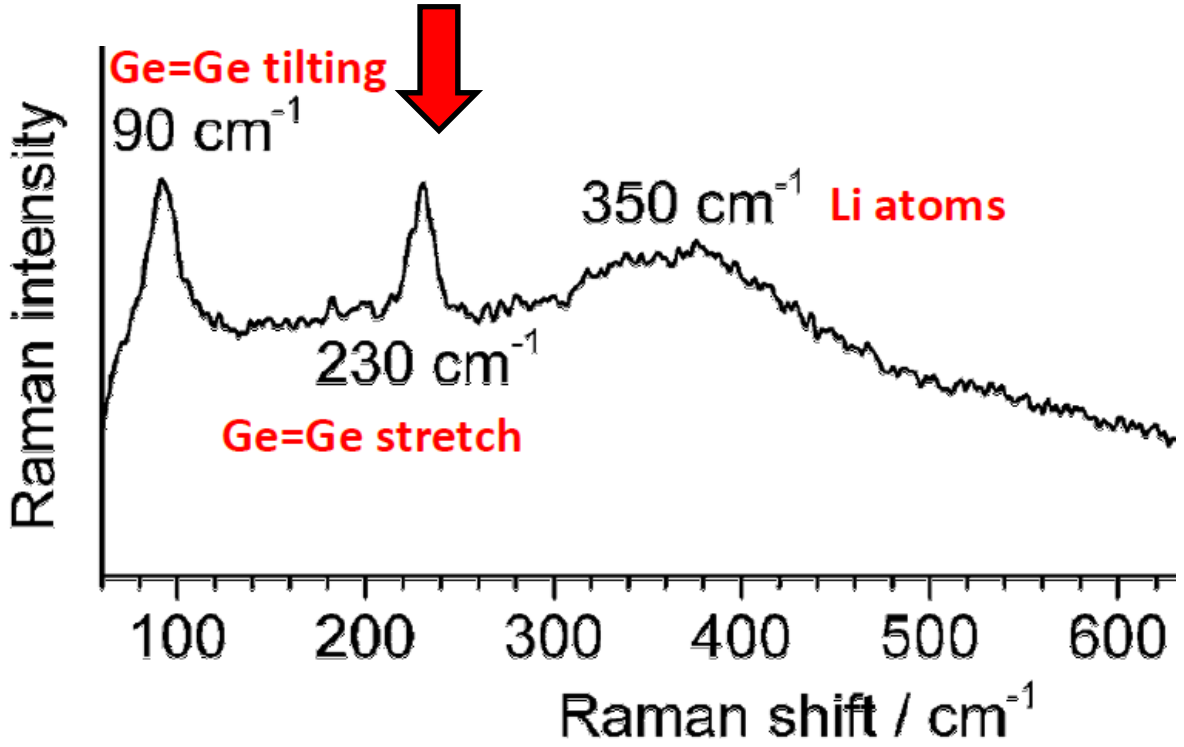
Ge–Ge bond distance in bulk α-Ge 2.45 Å





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])

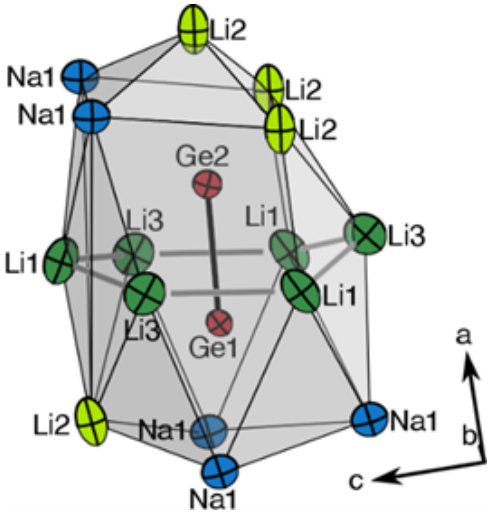
Raman Spectrum of a Li_3NaGe_2 Single Crystal

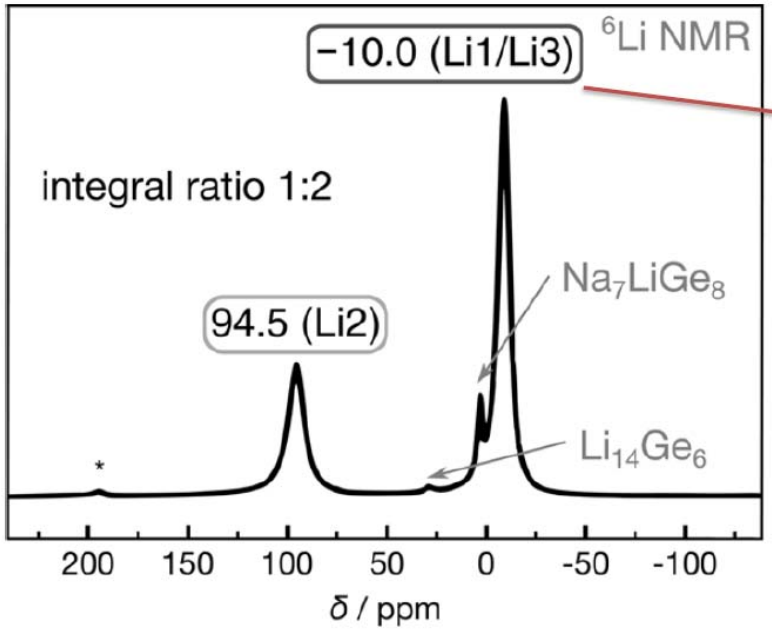


Assignment of the modes: Quantum chemical calculations

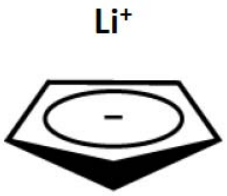
^{6}Li MAS NMR on Li_3NaGe_2

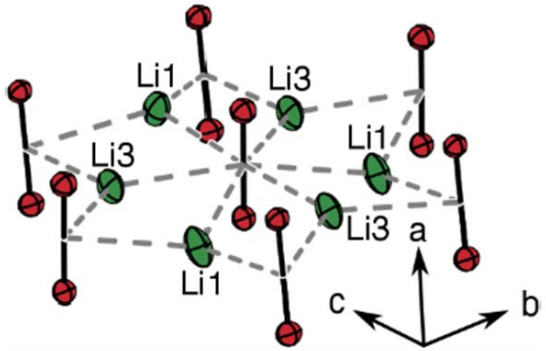
^{6}Li-enriched Li_3NaGe_2





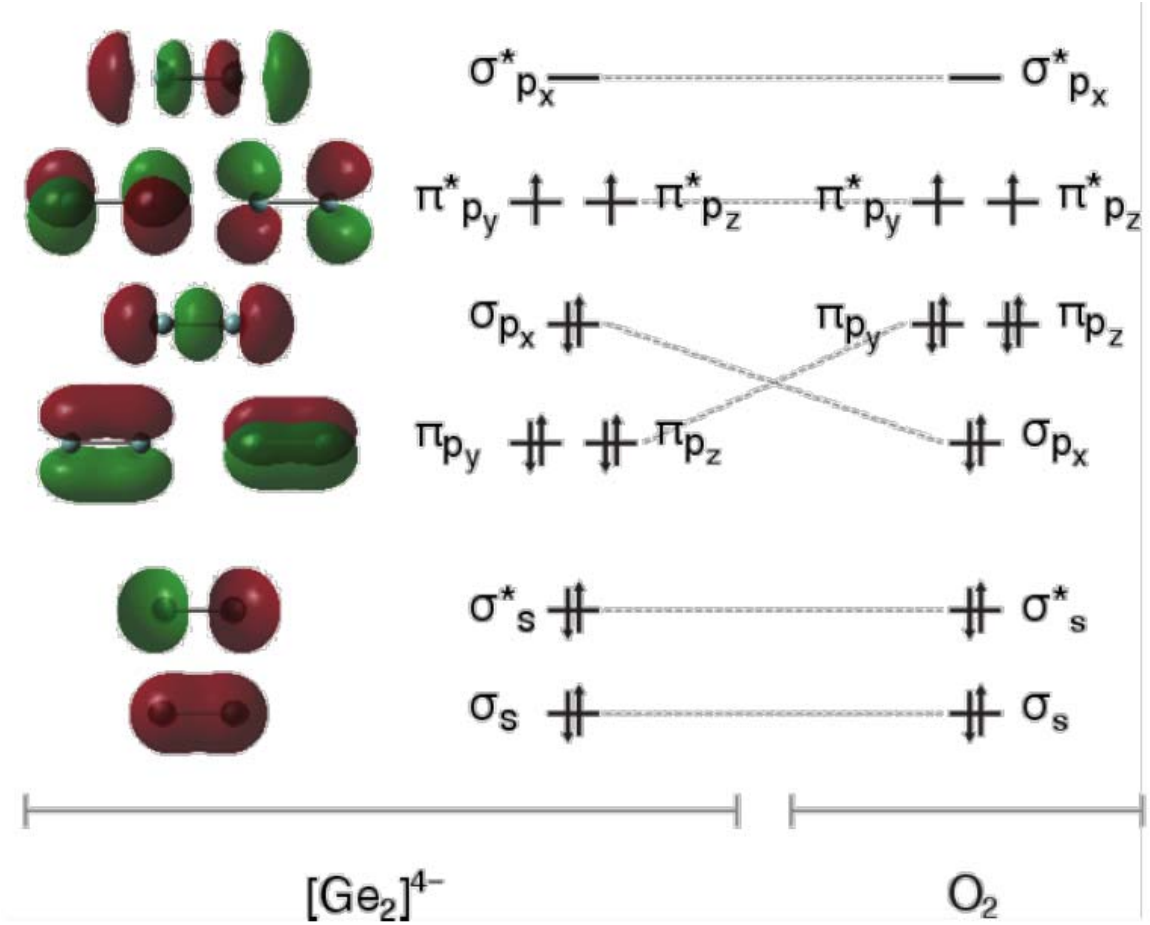
Negative shift, similar to π-coordinated Li^+ in for example $(Li^+)(Cp^-)$ with –7.6 ppm





Li1/Li3 surrounded by the π electrons of three Ge dumbbells – magnetic anisotropy of Ge=Ge – shielded signals

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

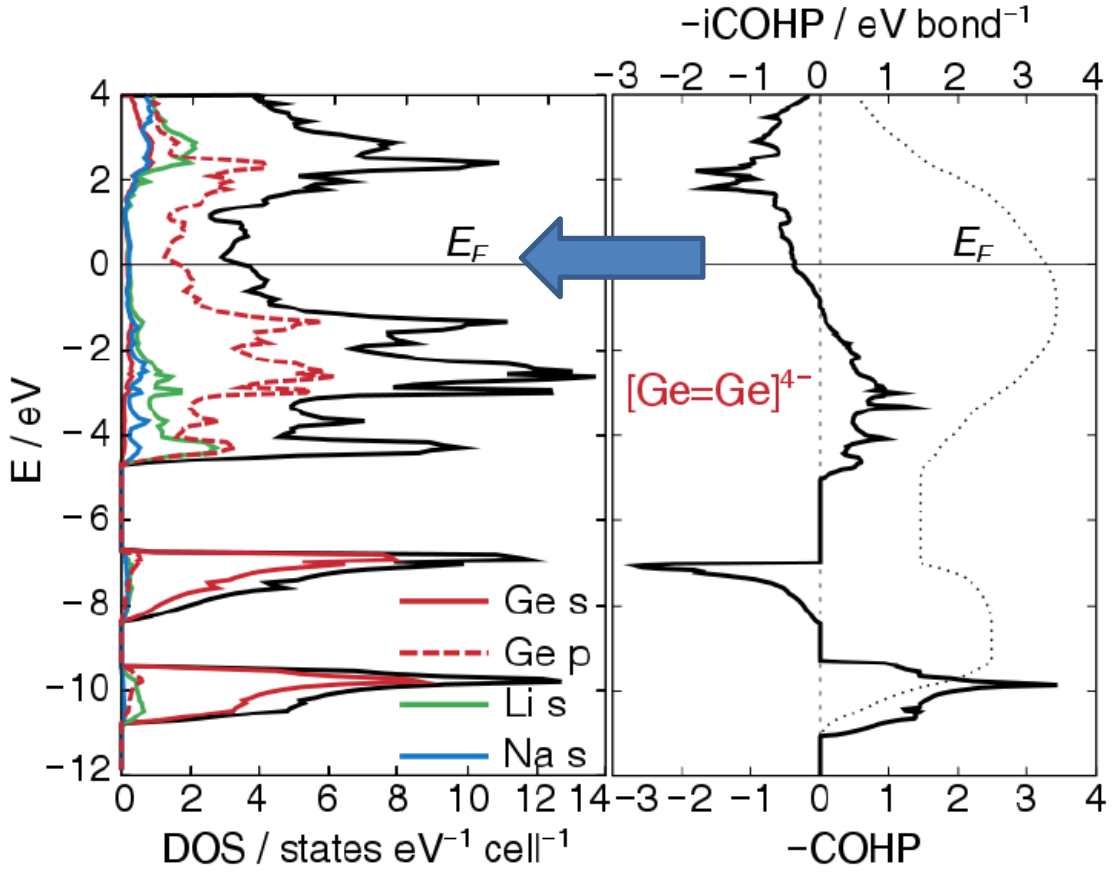


HOMO

Li_3NaGe_2 is not paramagnetic the partially filled bands in the solid state resulting in metallic properties

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

Band Structure Analysis



Unoccupied bands

Fermi level

Occupied bands

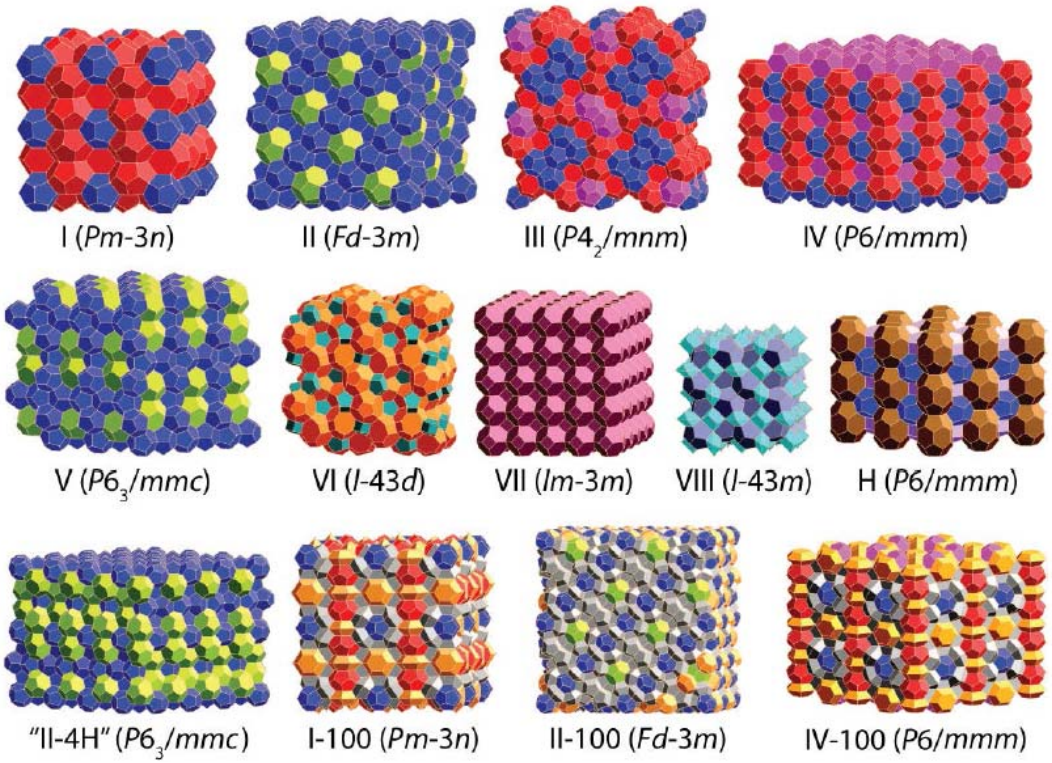
A significant density of states at the Fermi level – no band gap
Partially occupied π-antibonding **Ge(p)** orbitals

Metallic (conducting) solid

Diamagnetic

Clathrate Frameworks

Host lattice (4-coordinated frameworks) + **Guest** molecules/ions in the cavities



Hydrogen-bonded frameworks: hydroquinone, urea, thiourea

Methane clathrates - hydrogen-bonded framework of water and the methane guest

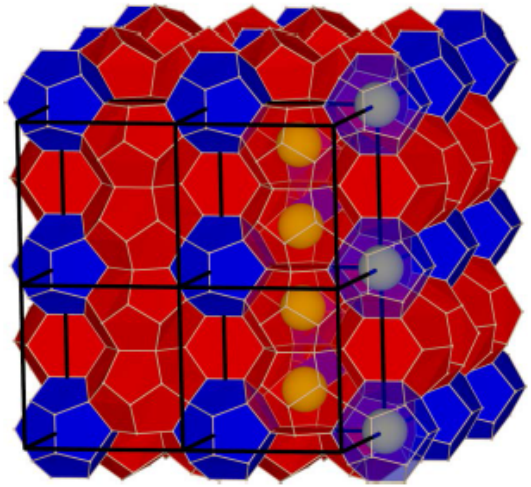
Covalent frameworks: zeolites, silica

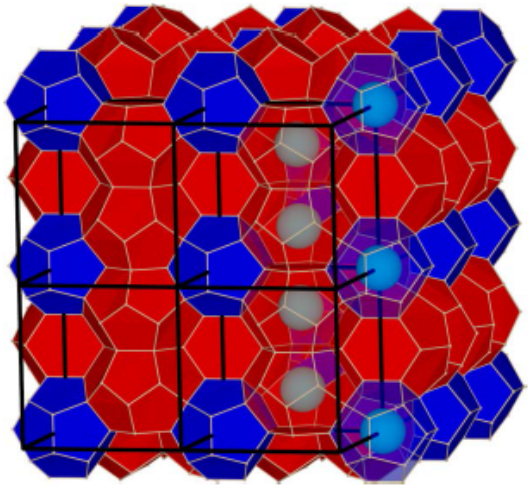
Coordination polymers: MOFs

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

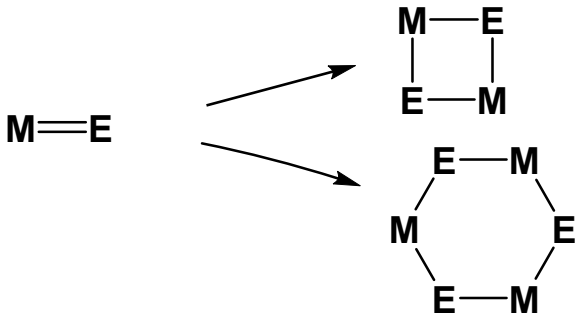
Polyhedral Cages

A large family of polyhedral molecules

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

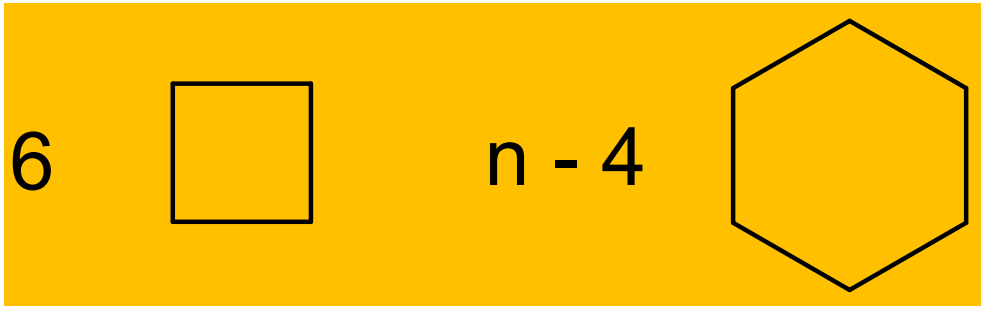
Contain **6 squares** and **(n – 4) hexagons**

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

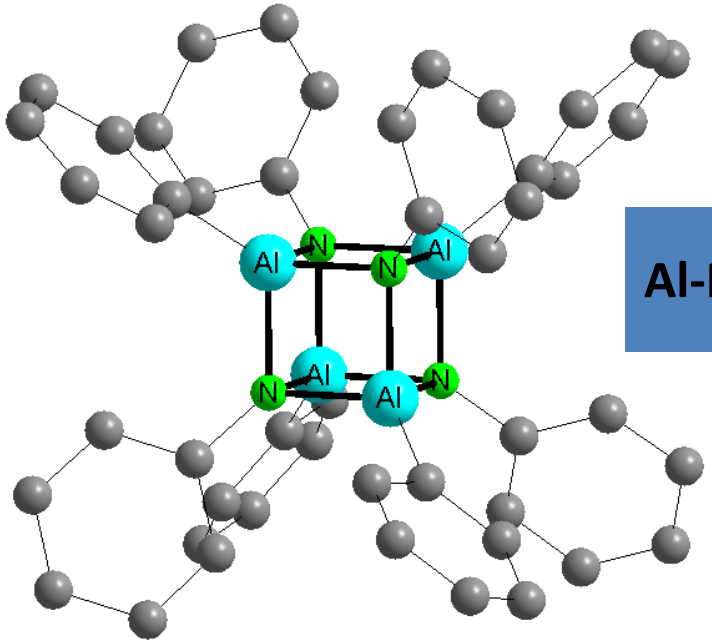


Iminoalanes $[R\text{-}Al{=}N\text{-}R']_n$

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



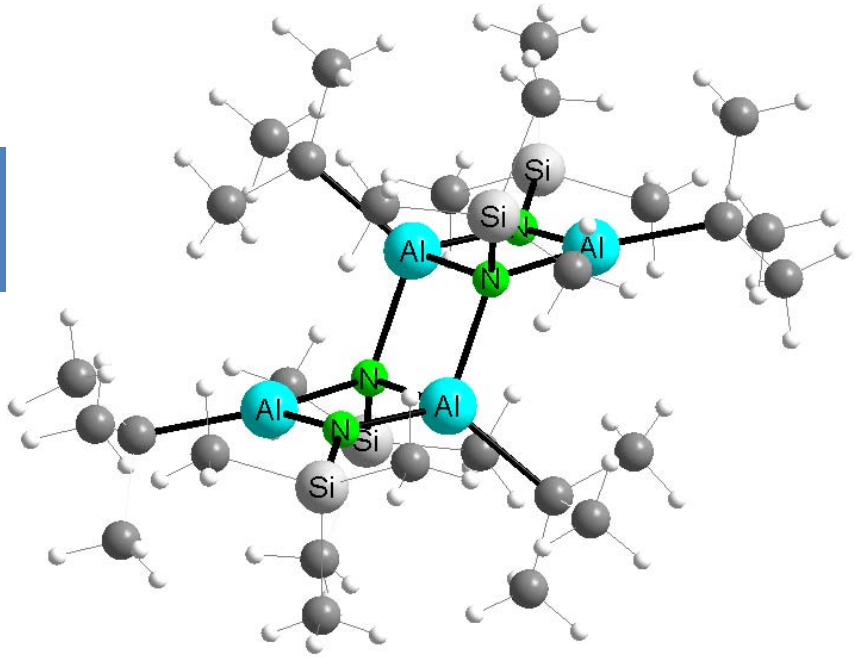
Polyhedral Cages n = 4



Al-N 1.95 Å

n = 4

(n – 4) hexagons = 0

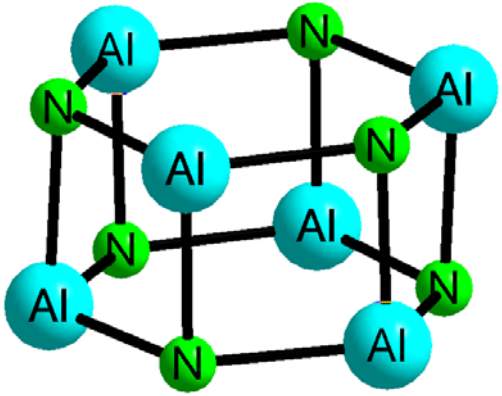


n = 4

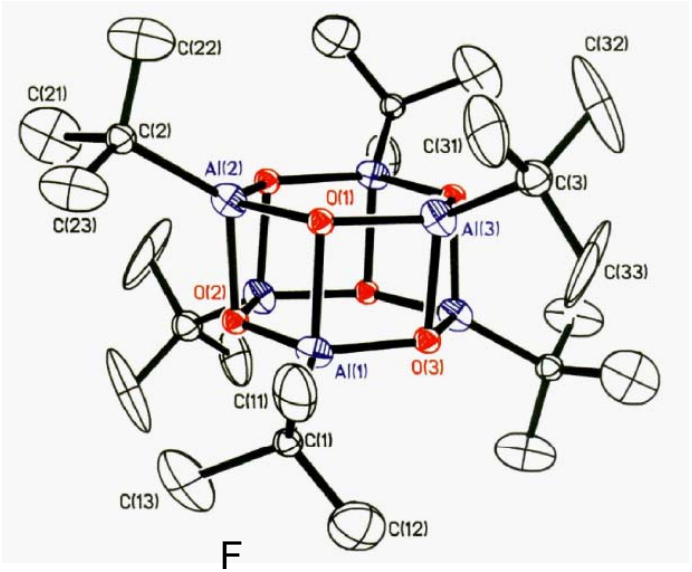
What is wrong?

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

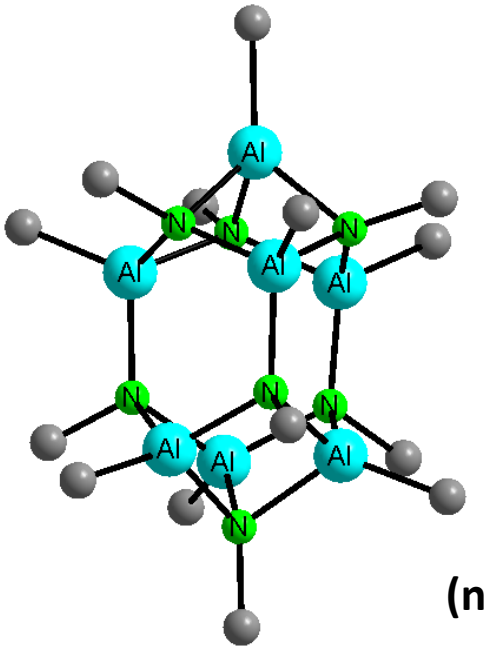
Polyhedral Cages n > 4



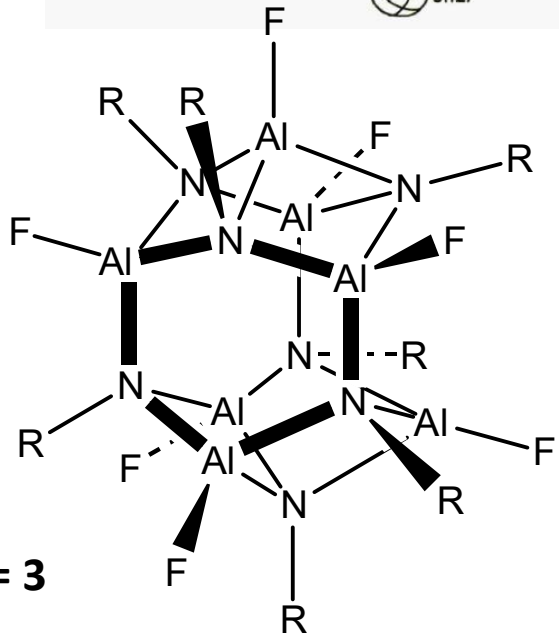
n = 6



(n – 4) hexagons = 2

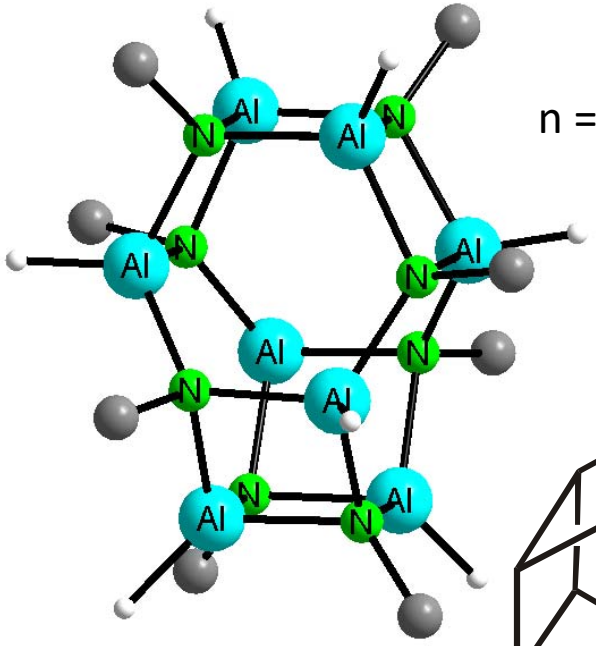


n = 7

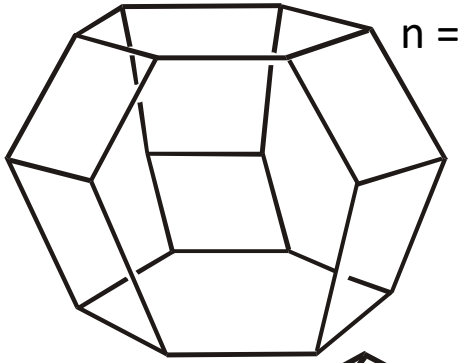


(n – 4) hexagons = 3

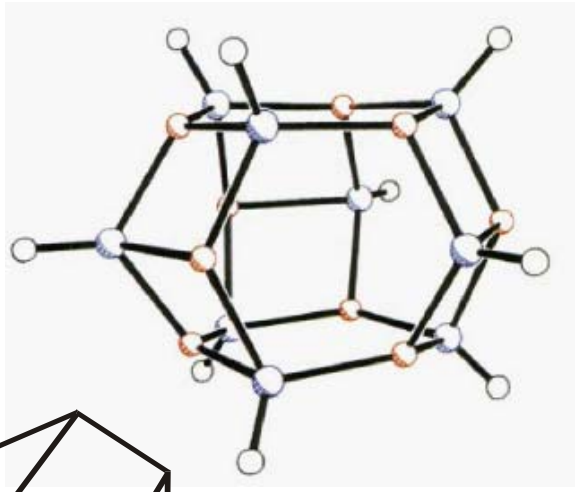
Iminoalanes $[RAlNR']_n$ n > 4

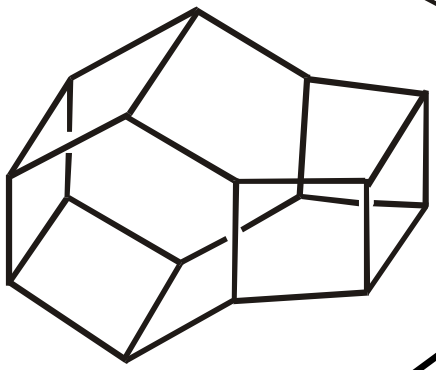


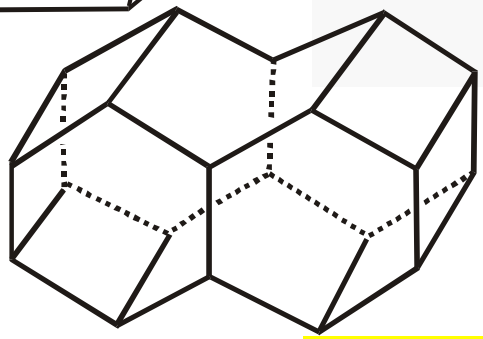
n = 8



n = 9

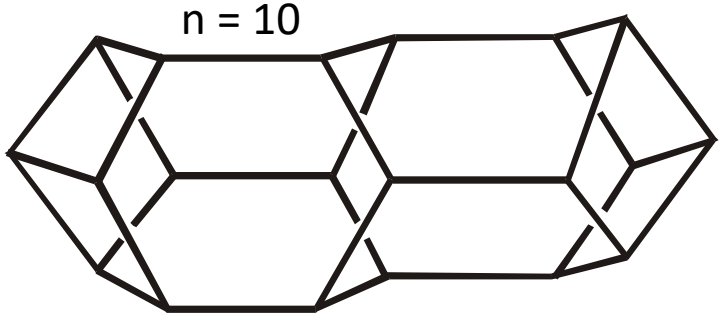


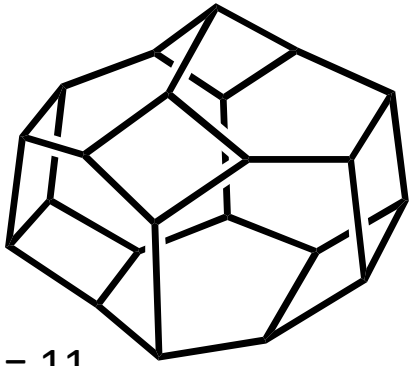




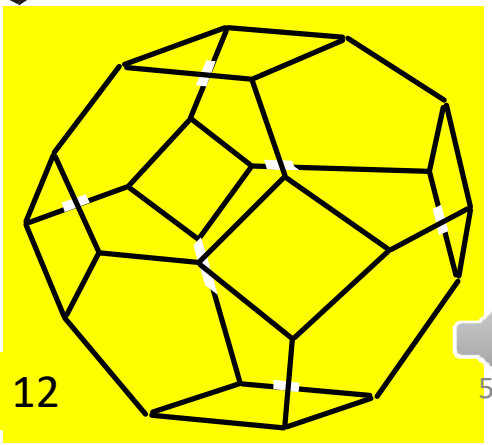
n = 10

n = 10



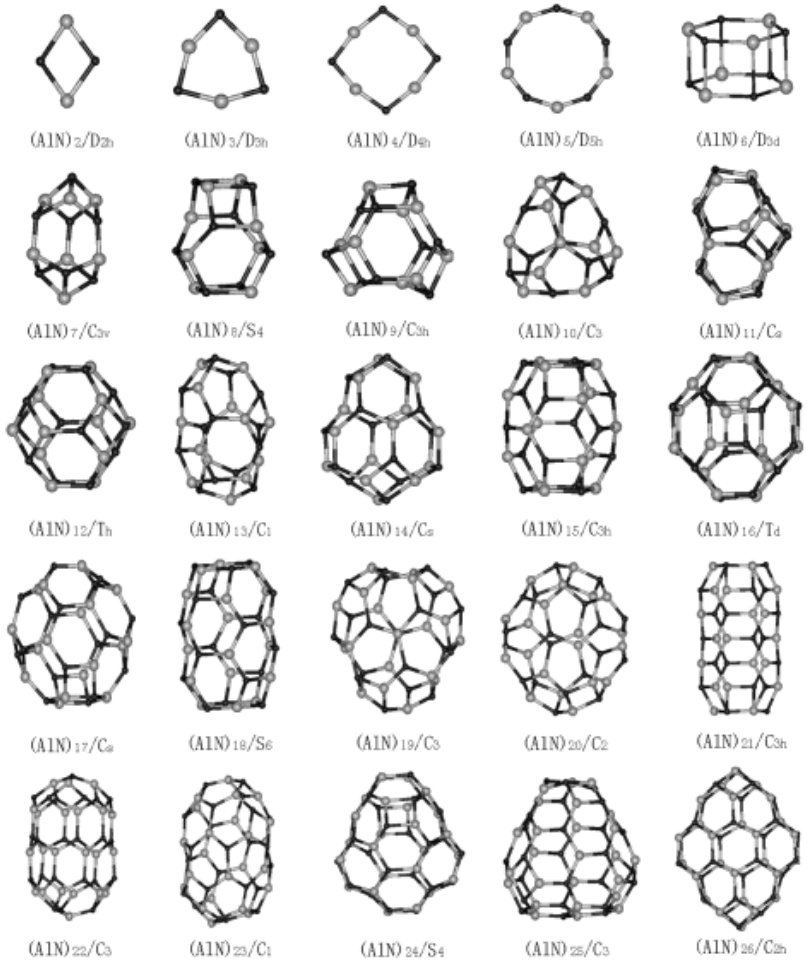


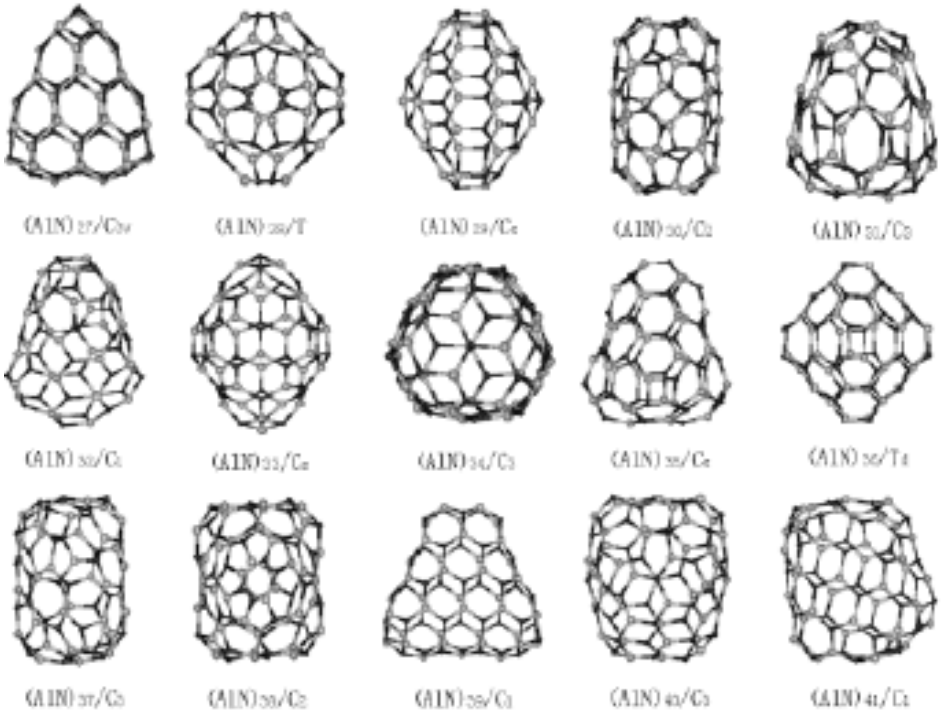
n = 11



n = 12

Most Stable $(AlN)_n$ Cages (n = 2–41)





$[R\text{-}Al{=}N\text{-}R']_n \rightarrow\rightarrow\rightarrow AlN$

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

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

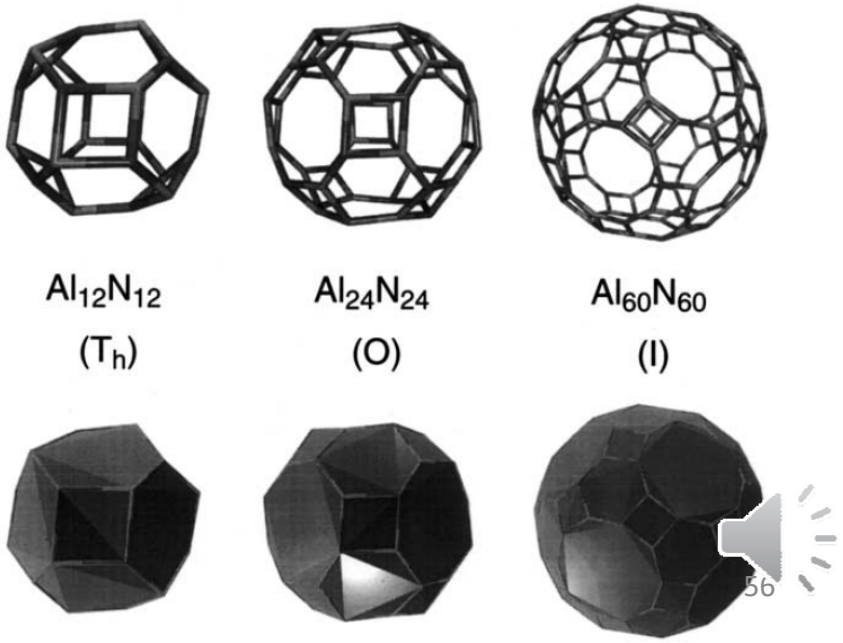
σ = 0–1

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

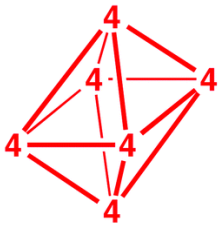
Kenneth Wade
1913-2014

Rules provide qualitative understanding of the **electron deficient multicenter bonding** of boron hydrides and their shape-based classification

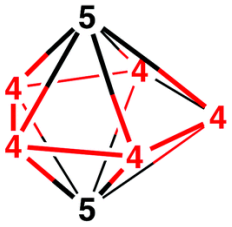
Wade's rule - a cage molecule with a geometry based on a deltahedron (closed polyhedron constructed of triangles = Δ) with ***n* vertices** will possess ***n* + 1 skeletal bonding electron pairs**

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	$B_5H_{12}^-$

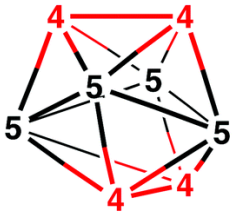
Deltahedra



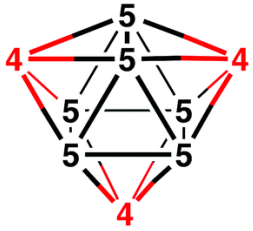
6 vertices:
Octahedron



7 vertices:
Pentagonal
Bipyramid

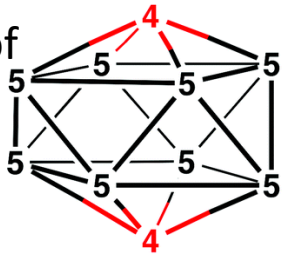


8 vertices:
Bisdisphenoid
("D_{2d} Dodecahedron")

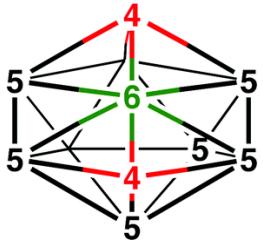


9 vertices:
4,4,4-Tricapped
Trigonal Prism

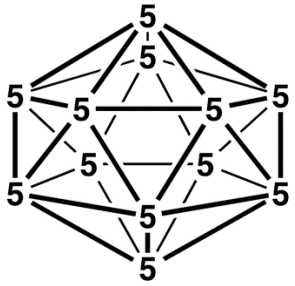
Deltahedra = closed polyhedra constructed of triangular faces



10 vertices:
4,4-Bicapped
Square Antiprism



11 vertices:
Edge-coalesced
Icosahedron

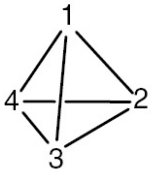


12 vertices:
Icosahedron

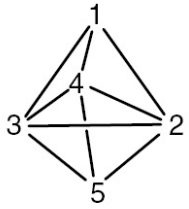
Euler's rule: f + v = c + 2

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

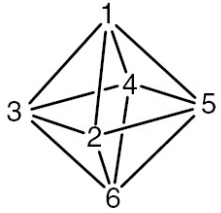
Deltahedra



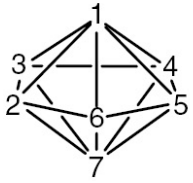
tetrahedron
closo 4-vertex



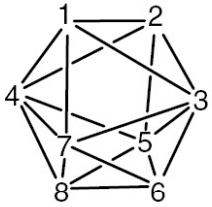
trigonal bipyramid
closo 5-vertex



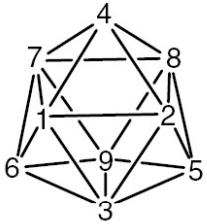
octahedron
closo 6-vertex



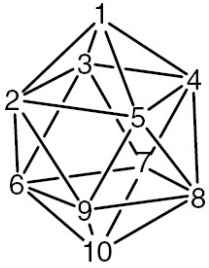
pentagonal bipyramid
closo 7-vertex



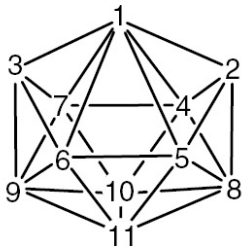
dodecahedron
closo 8-vertex



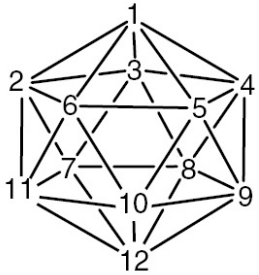
tricapped trigonal prism
(tetradecahedron)
closo 9-vertex



bicapped square antiprism
(hexadecahedron)
closo 10-vertex

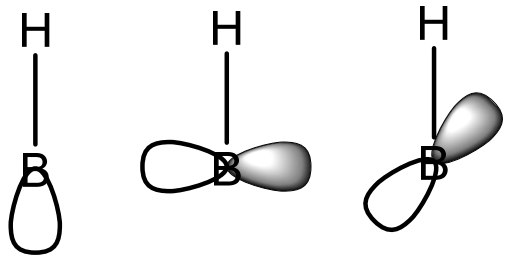


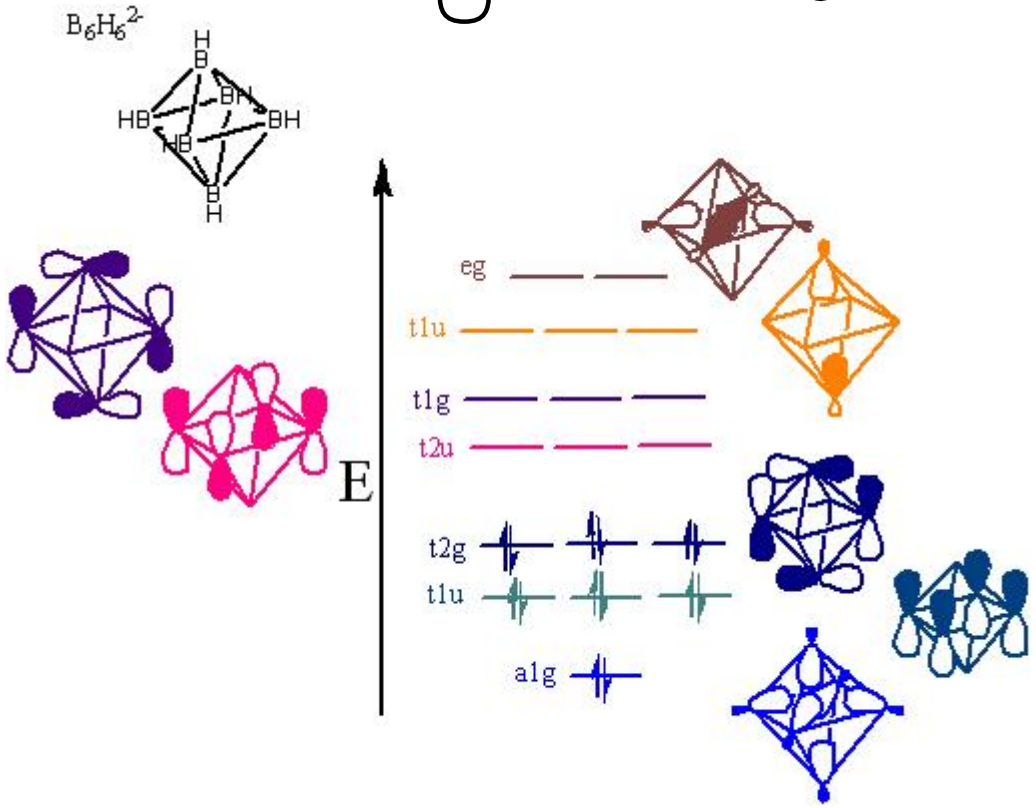
octadecahedron
closo 11-vertex



icosahedron
closo 12-vertex

Deltahedral Boranes





Electron deficient molecules
Each B = 3 electrons

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

- Exoskeletal B–H bonds
- Endoskeletal bonding:

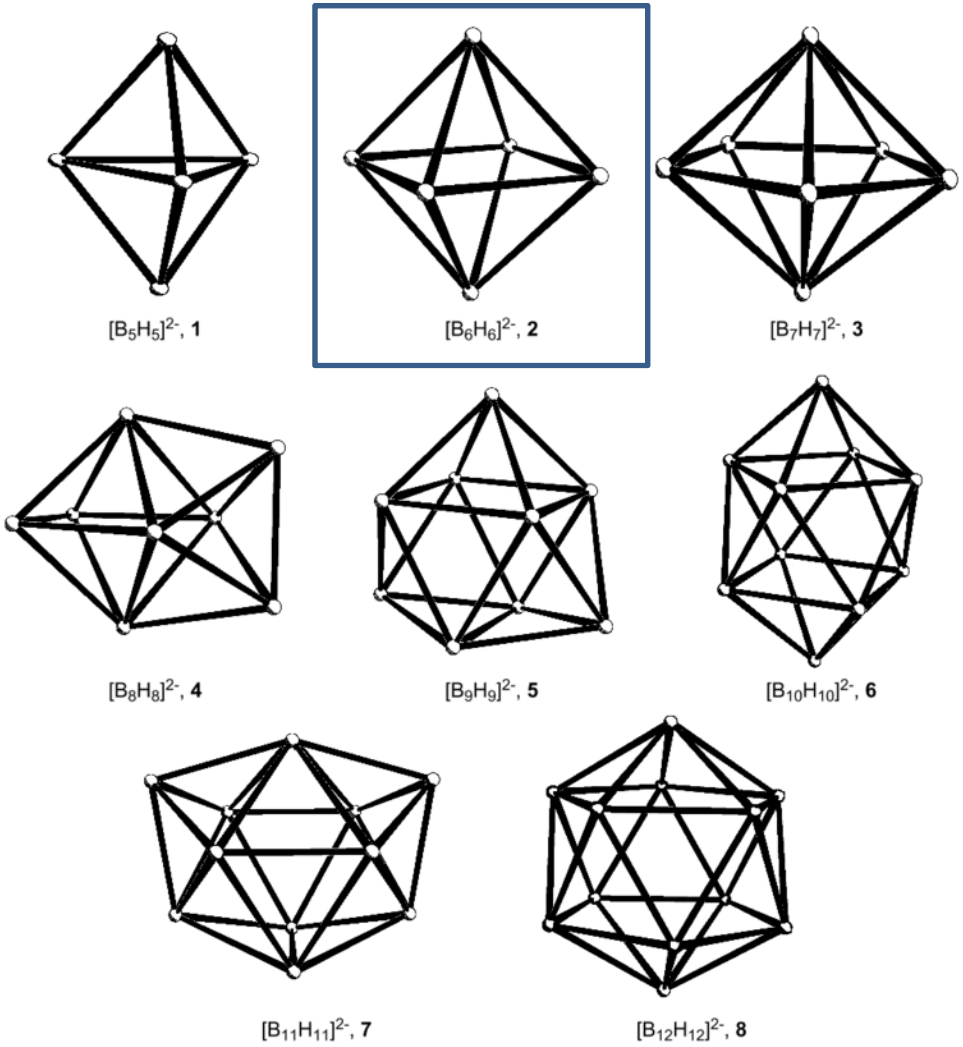
n axial orbitals combine to **1 bonding** and **n–1** antibonding MO

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

n + 1 bonding MO

2n + 2 **skeletal bonding electron**

Deltahedral Boranes



n + 1 bonding MO

n + 1 skeletal bonding electron pairs - Wade's rule

Need 2n + 2 skeletal bonding electrons = 14 e

$B_6H_6^{2-}$

6 B = 6 × 2 e = 12 e
Charge 2− = 2 e

Total = 14 e

Wade's Rules

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

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

$$E = v + x - 2$$

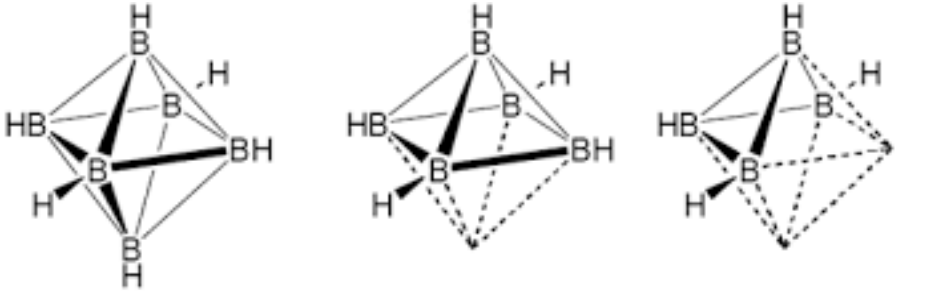
v = number of valence electrons
x = number of electrons from ligands: Cl, F, H = 1, Lewis base = 2

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

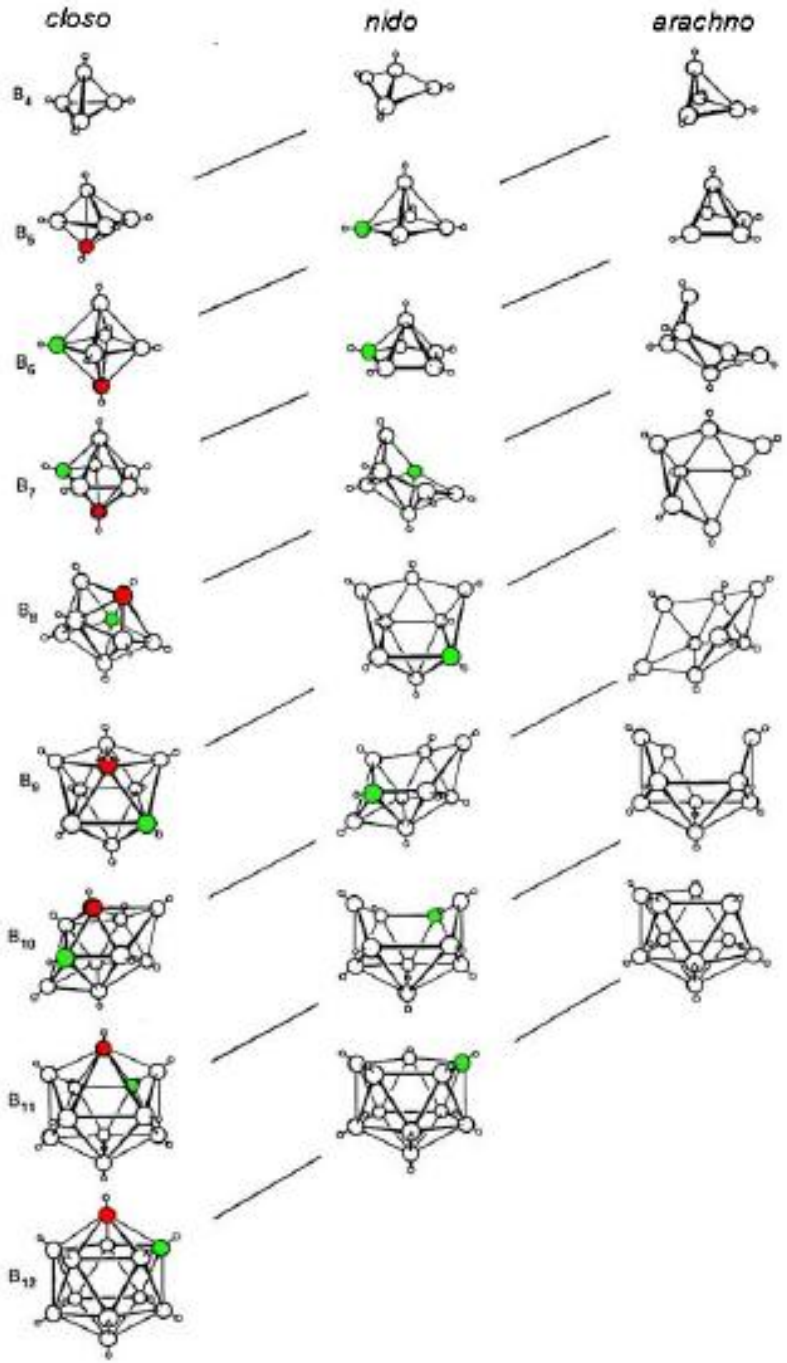
Wade's Rules

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 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



Wade's Rules

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

Boron hydride	Name	No. of skeletal electron pairs
$[B_nH_n]^{2-}$ or B_nH_{n+2}	Closo	n+1
B_nH_{n+4}	Nido	n+2
B_nH_{n+6}	Arachno	n+3
B_nH_{n+8}	Hypho	n+4

Wade's Rules

Classify the structure of **B_5H_{11}** (= $B_5H_5^{6-}$)

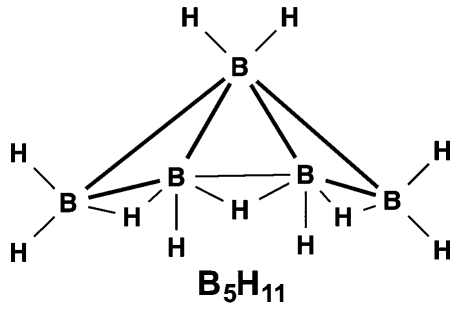
Total number of valence electrons = (5 x B) + (11 x H) = (5 x 3) + (11 x 1) = 26 e
Number of electrons needed for each B-H bond = (5 x 2) = 10 e

Number of available **skeletal electrons** = 26 – 10 = 16 e

Number of **skeletal bonding electron pairs** = 16/2 = 8

n = 5 boron atoms and n + 3 = 8 skeletal bonding electron pairs

B_5H_{11} is an *arachno* based upon a pentagonal bipyramid with two apexes missing



Wade's Rules

Classify the structure of **B_5H_9**

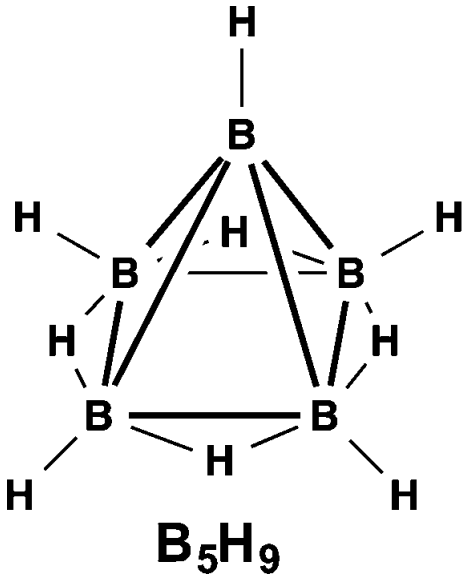
Total number of valence electrons = (5 x B) + (9 x H) = (5 x 3) + (9 x 1) = 24 e
Number of electrons for each B-H unit = (5 x 2) = 10 e

Number of skeletal electrons = 24 – 10 = 14 e

Number skeletal bonding electron pairs = 14/2 = 7

n = 5, n + 2 = 7

B_5H_9 is a *nido* structure based upon an octahedral structure with one apex missing



B_5H_9

Jemmis' *mno* Rules

E.D. Jemmis
IISc Bangalore

***m + n + o* skeletal electron pairs are necessary for a closed macropolyhedral system to be stable**
or (*m + n + o + p*) for systems having open polyhedra as well

m = number of condensed polyhedra
n = number of vertices
o = number of single atom bridges between two polyhedra
p = number of vertices missing for open polyhedra if present

Jemmis' rules get reduced to Wade's rules when m = 1 and o = 0 (one polyhedron)

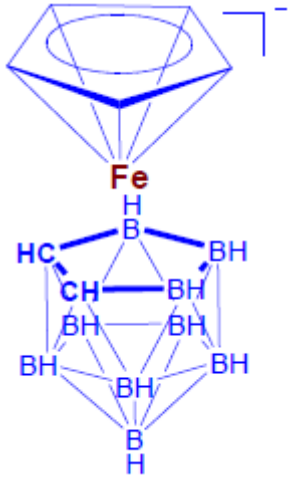
For example, for nido clusters *p* = 1 and for arachno clusters *p* = 2
For a benzene ring or cyclopentadienyl ring as such *p* = 2 and if it is in an η^6 or η^5 mode, p = 1

Jemmis' *mno* Rules

Jemmis' mno rules are not only applicable to macropolyhedral clusters but also applied to polyhedra, metallocenes, and even unsaturated cyclic organic compounds

Thomas P. Fehlner

For transition metals, the oxidation state should be known and the number of e for the electron count is the number of electrons lost by the neutral metal atom; for example, Fe^{3+} gives 3 e, Fe^{2+} gives 2 e



Jemmis

m = number of condensed polyhedra = 2

n = number of vertices = 17

o = number of single atom bridges (Fe) between two polyhedra = 1

p = number of vertices missing for open polyhedra (nido) = 1

m + n + o + p = 2 + 17 + 1 + 1 = **21 skeletal electron pairs**

Skeletal e count

9 BH = 2 × 9 = 18 e

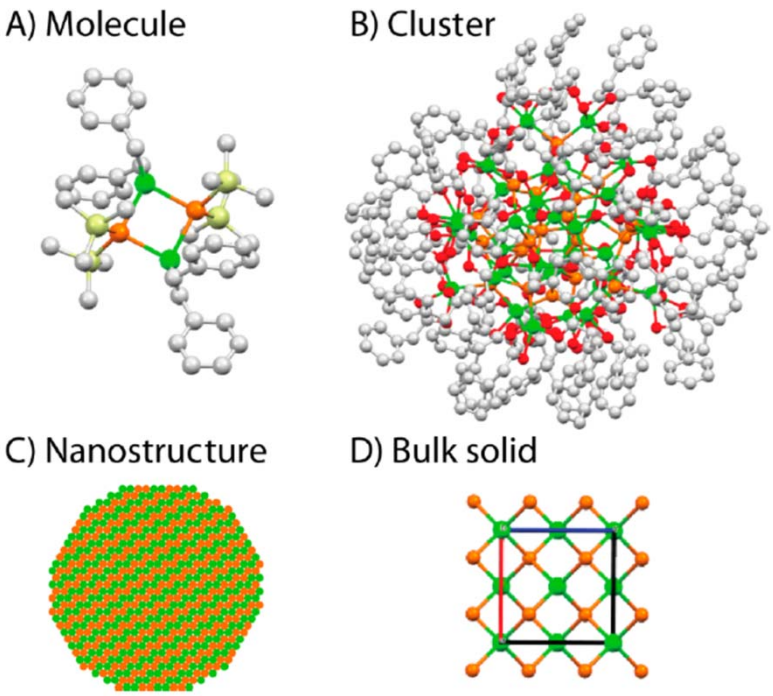
2 + 5 CH = 3 × 7 = 21 e

Fe^{2+} = 2 e (Cp 1–, carborane 2–)

Charge 1– = 1 e

Total 42 e = **21 skeletal electron pairs**

Atomically Precise Clusters



Over 100 molecules with formulas such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, $Au_{102}(SR)_{44}$, $Ag_{25}(SR)_{18}$, $Ag_{29}(S2R)_{12}$, and $Ag_{44}(SR)_{30}$

Superatom model “jellium”
Electrons confined within a spherically symmetric potential well of the metal core

If the number of free electrons is the “**magic**” number (2, 8, 18, 20, 34, 58, ...), the cluster shows high **stability**

Chem. Rev. 2017, 117, 8208−82, 10.1021/acs.chemrev.6b00769

Atomically Precise Clusters

Electron counting

$N_s = N \nu_A - L - q$

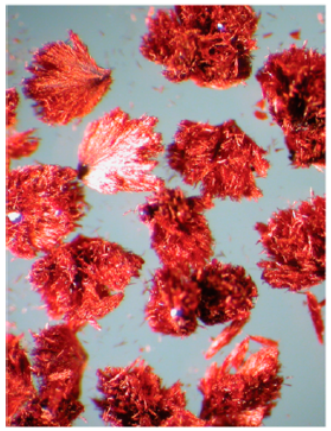
N_s - the shell closing number (free electron count)

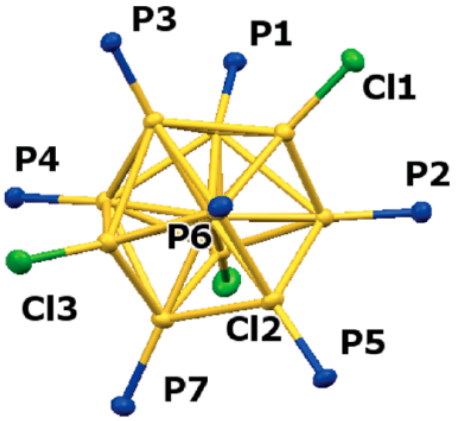
N - the number of core metal atoms
ν_A - the effective valence electrons (for Au/Ag, $v_A = 1$)
L - the number of one-electron withdrawing ligands
q - the total charge (+q or −q) on the cluster

Two-electron ligands (phosphine, amine) do not withdraw electrons; a dative bond, do not get counted

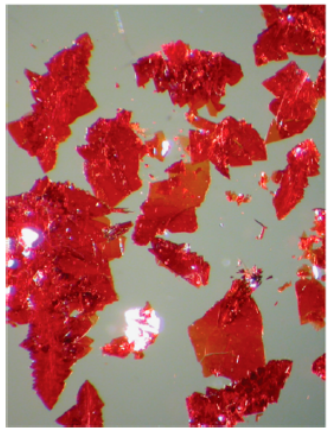
Atomically Precise Clusters

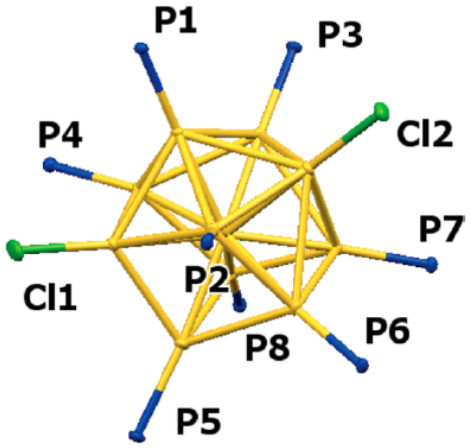
$Au_{11}(PPh_3)_7Cl_3$ (needles)

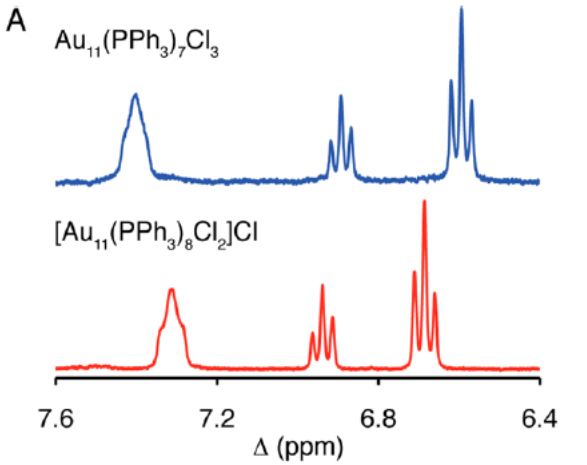


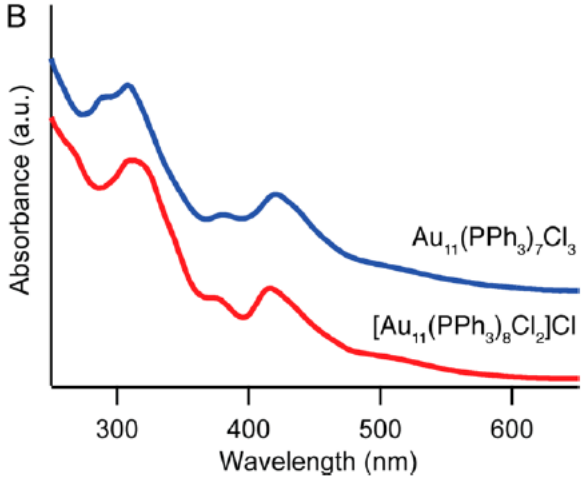


$[Au_{11}(PPh_3)_8Cl_2]Cl$ (plates)









J. Am. Chem. Soc. 2014, 136, 13426, 10.1021/ja5075689