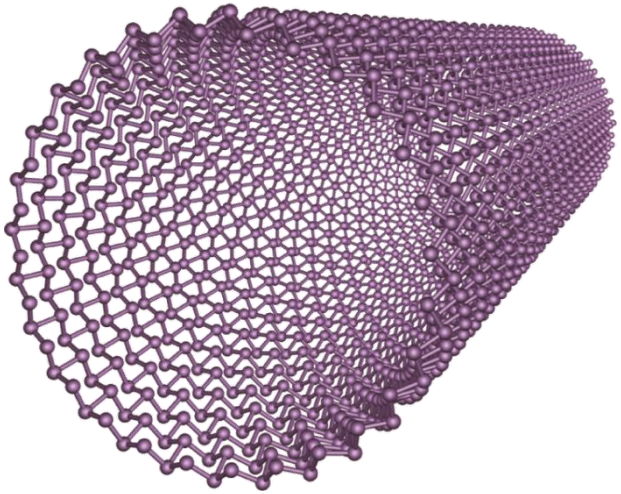
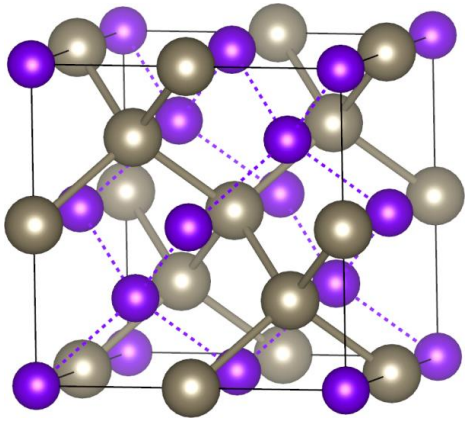
Lecture 10:
Main group compounds

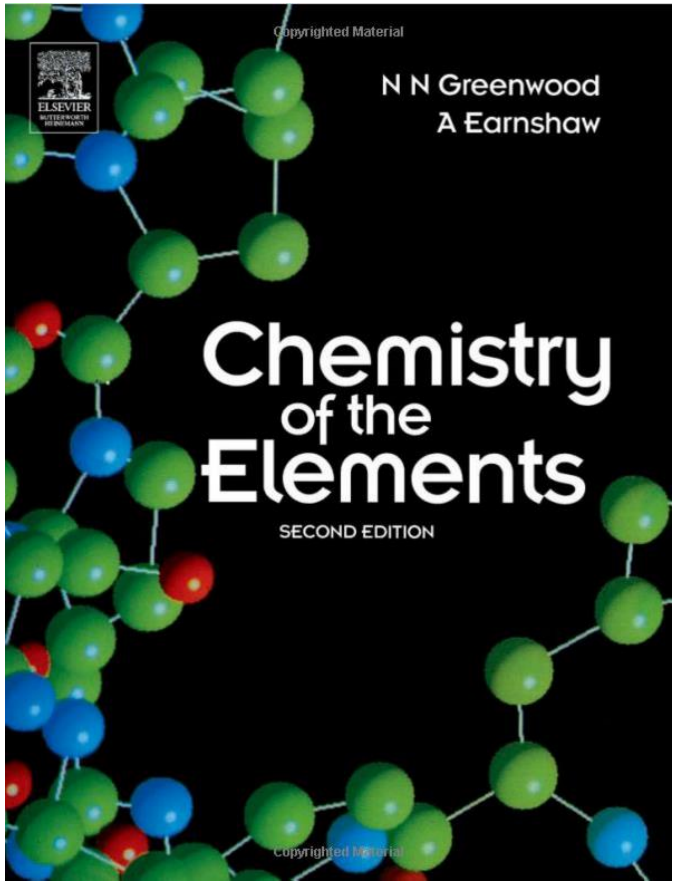
- Some general trends and classifications for non-molecular main group compounds
- Allotropes
  - Group 14 elements
  - Group 15 elements
  - Group 16 elements
- Zintl phases
  - General principles
  - Typical examples
  - Semiconducting clathrates
  - Li_3NaGe_2





Figures: AJK

Literature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N N Greenwood
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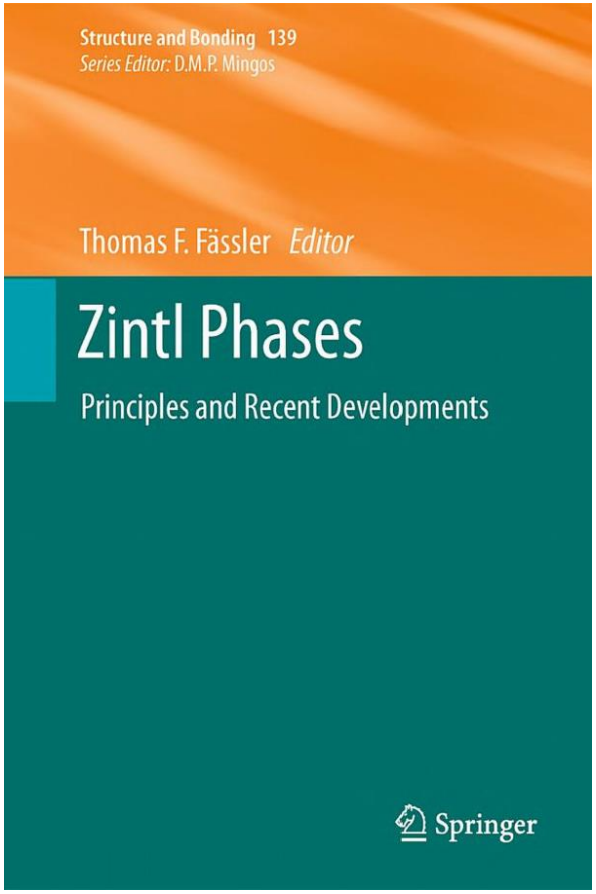
Structure and Bonding 139
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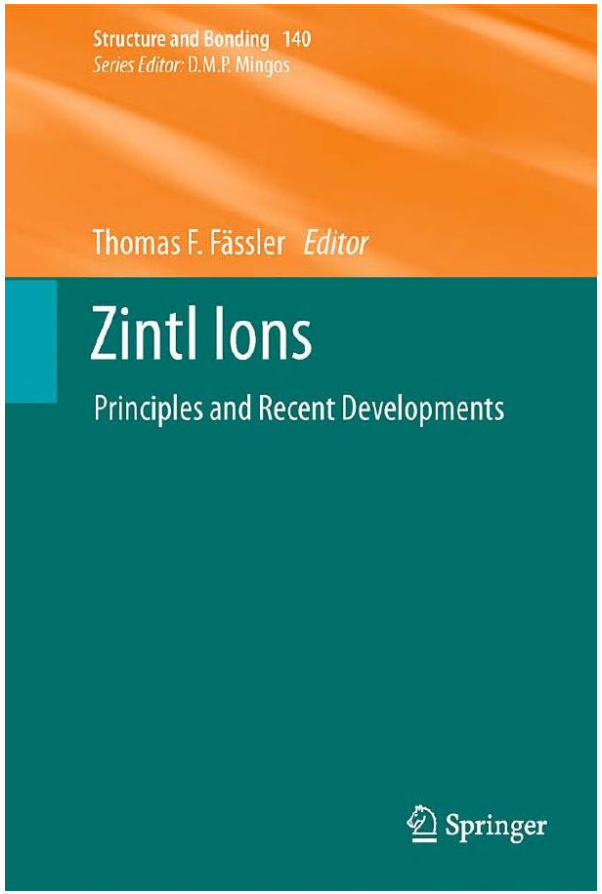
Zintl Phases
Principles and Recent Developments
Springer


Structure and Bonding 140
Series Editor: D.M.P. Mingos
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Zintl Ions
Principles and Recent Developments
Springer

Main group elements

V·T·E

Periodic table of electronegativity by Pauling scale

→ **Atomic radius** decreases → **Ionization energy** increases → **Electronegativity** increases →

Group → / ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27
**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3

Metal/metalloid line

Figure: Wikipedia

Overview of main group compounds (1)

- Group 1+2 compounds
  - Not so relevant, but some interesting examples such as Laves phase $CaLi_2$
- Groups 1 + 17 and groups 2 + 17
  - Typically simple salts (discussed previously)
- Halides known practically for all main groups 13-15
  - Mostly molecular for B, C, Si, Ge, Sn, group 15, and group 16
  - Mostly non-molecular for Al, Ga, In, Tl, Pb
  - Almost follows metal/metalloid line
- Oxides
  - Simple salts for groups 1 and 2
  - Stable oxides for groups 13-16, not 17
  - Vast number of minerals
- Other chalcogenides (S, Se, Te)
  - Similarly to O, chalcogenides known practically for all main group elements (groups 1, 2, 13-15)

Figure: Wikipedia/AJK

Periodic table of electronegativity by Pauling scale

1	2	13	14	15	16	17
H 2.20						
Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66
Cs 0.79	Ba 0.89	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Uut	Fl	Uup	Lv	Uus

$CaLi_2$ Laves phase ($P6_3/mmc$)

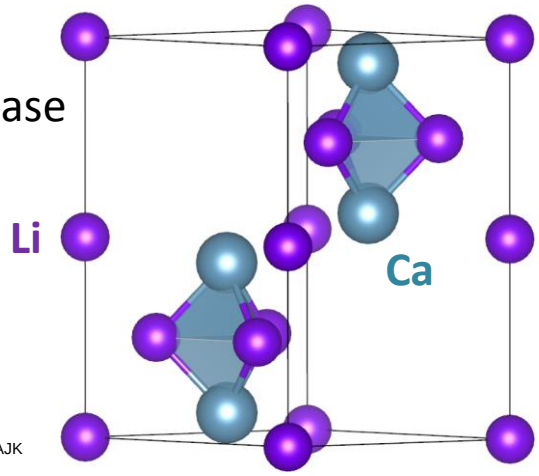

Figure: AJK

Overview of main group compounds (2)

- Group 1/2 + 14: Carbides, silicides, germanides, …
  - CaC_2, Mg_2Si, $CaGe_2$, ...
- Group 1/2 + 15: Nitrides, phosphides, arsenides, …
  - Li_3N, Li_3P, Li_3As, …
- Main group compound semiconductors
  - 13-15 (BN, GaN, GaAs, etc.)
  - 14-16 (PbTe, PbSnTe, SnS, etc.)
  - 15-16 (Sb_2Se_3, Bi_2Te_3, etc.)
- Some elements are technologically extremely important as such or as simple alloys/compounds
  - Si, Ge, Si_xGe_{1-x}, SiC (semiconductors)
  - Al and Mg as structural metals

Periodic table of electronegativity by Pauling scale

1	2	13	14	15	16	17
H 2.20						
Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
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K 0.82	Ca 1.00	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66
Cs 0.79	Ba 0.89	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Uut	Fl	Uup	Lv	Uus

Figure: Wikipedia/AJK

Focus of the lecture: Allotropes and Zintl phases

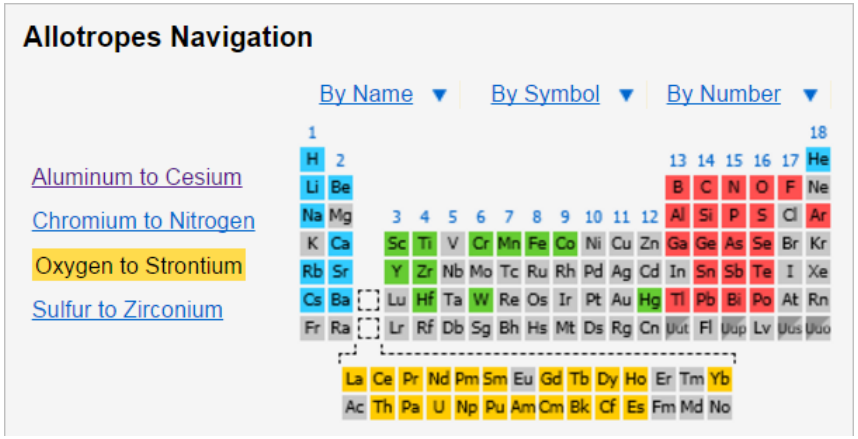
- Several main group elements show very rich ***allotropy*** in ambient pressure
  - Different structural modifications of the same element (IUPAC Gold Book)
  - Highly interesting from fundamental scientific point of view, but also of high technological relevance (for example, allotropes of carbon)
  - Here we consider ***atmospheric pressure*** only!
- ***Zintl phases*** are an important class of main group compounds with connections to G14-16 allotropes
  - Include semiconductors with applications in thermoelectrics, etc.
- Key concept for the lecture: ***isoelectronic principle***
  - Same number of valence electrons and the same structure, *i.e.* number and connectivity of atoms, but different composition (CO / N_2)

13	14	15	16
B	C	N	O
Al	Si	P	S
Ga	Ge	As	Se
In	Sn	Sb	Te
Tl	Pb	Bi	Po

Main groups 13-16, elements showing allotropy highlighted

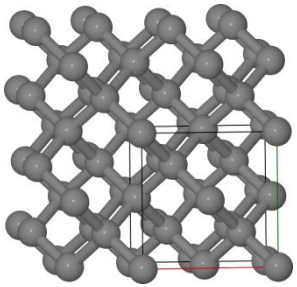
Allotropy

- Knowledgedoor.com has a good listing of allotropes with original references
  - http://www.knowledgedoor.com/2/elements_handbook/allotropes.html
- Note that many are for high pressure
- ”Textbook”-level information, the most recent research not included
- http://www.knowledgedoor.com/ is actually a rather good source of physical data (references to original data available)
- Let’s see few examples of group 14, 15, and 16 allotropes

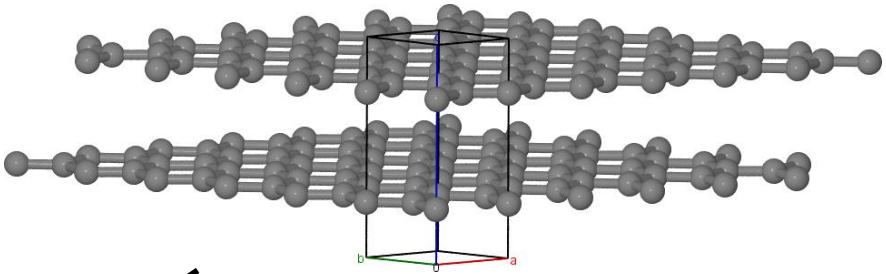


Carbon	
allotrope category	diamond
allotrope	cubic diamond
allotrope	hexagonal diamond
alternate name	lonsdaleite
allotrope category	graphite
allotrope	hexagonal graphite
alternate name	α-graphite
allotrope	rhombohedral graphite
alternate name	β-graphite
allotrope	turbostratic graphite
allotrope	chaoite
allotrope category	fullerenes
allotrope	fullerene-C_{60}
symbol	C_{60}
allotrope	fullerene-C_{70}
symbol	C_{70}
allotrope	carbon nanotubes
allotrope	carbon onions
allotrope	carbon fibers
allotrope	carbon foams
allotrope	graphene films
allotrope	carbon black

The allotropy of carbon



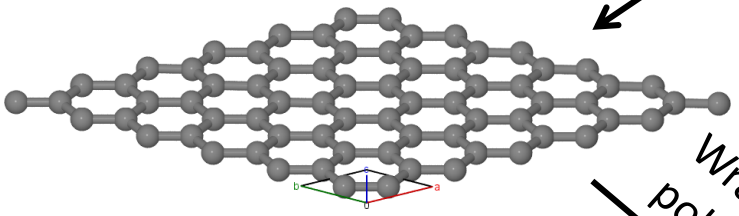
3D allotropes



Diamond (sp^3 bonding)

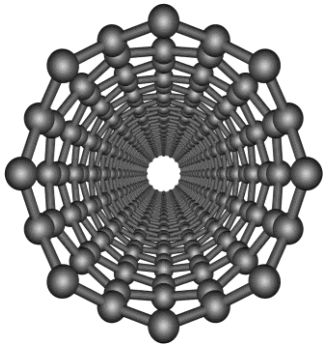
Graphite (sp^2 bonding)

Cut a slab



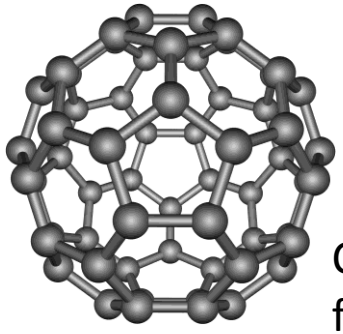
Graphene (2D)

Roll up to a tube



Carbon nanotube (1D)

Wrap up to a polyhedron



Carbon fullerene (0D)

Figure: AJK

The allotropy of silicon

- Short overview available in: A. J. Karttunen, D. Usvyat, M. Schütz, L. Maschio, Dispersion interactions in silicon allotropes, *Phys. Chem. Chem. Phys.* **2017**, *19*, 7699 (DOI: 10.1039/c6cp08873b)

Table 1 Silicon allotropes included in this study. The structures are ordered according to their relative energy ΔE at the LMP2/TZVPP level (see below) from the most to the least stable structure

Pearson[a]	Name(s)[b]	Space group	a^c (Å)	b^c (Å)	c^c (Å)	k-Grid[d]	Notes
*cF*8	Alpha (α)/3C	$Fd\bar{3}m$	5.43			12 × 12 × 12	Diamond structure. Most stable Si allotrope under STP conditions.
*hP*8	4H	$P6_3/mmc$	3.83		12.59	12 × 12 × 4	Hexagonal polytype of 3C. 4H-Ge has been synthesized as a bulk material starting from *m-allo*-Ge.[62,63]
*hP*4	2H	$P6_3/mmc$	3.83		6.32	12 × 12 × 6	Hexagonal polytype of 3C. 2H-Si has been fabricated on GaP nanowire templates.[64]
*tP*12	cdp/T12	$P4_2/ncm$	5.19		9.24	8 × 8 × 4	Hypothetical allotrope, topology the same as in CdP_2.[16,65]
*oP*32	GAa4	*Pbcm*	7.85	11.29	7.45	4 × 4 × 4	The most stable building block of stacking-faulted *m-allo*-Ge (synthesized as a bulk material structure starting from Li_7Ge_{12}).[17,63]
*hP*6	unj/NGS	$P6_122$	5.44		5.08	8 × 8 × 8	Hypothetical allotrope, topology the same as for the Ga–Sn network in $NaGaSn_5$.[17,66]
*tP*24	tum1	$P4_2/nmc$	7.42		9.15	6 × 6 × 4	Hypothetical allotrope, topology the same as for the B–Si network in $LiBSi_2$.[67]
*oC*24	CAS	*Cmcm*	3.82	10.68	12.66	8 × 8 × 4	Has been synthesized from Na_4Si_{24}.[68]
*cF*136	Clathrate II	$Fd\bar{3}m$	14.65			4 × 4 × 4	Has been synthesized from Na_xSi_{136},[4,5] also known for Ge.[7]
*cI*46	Clathrate VIII	$I\bar{4}3m$	10.04			4 × 4 × 4	Hypothetical allotrope, experimentally known in type-VIII Ge and Sn clathrates.[13,69,70]
*cP*46	Clathrate I	$Pm\bar{3}n$	10.16			4 × 4 × 4	Hypothetical allotrope, experimentally known in Na_8Si_{46} type-I clathrate.[13,69,70]

Open-framework allotrope of Si

nature materials

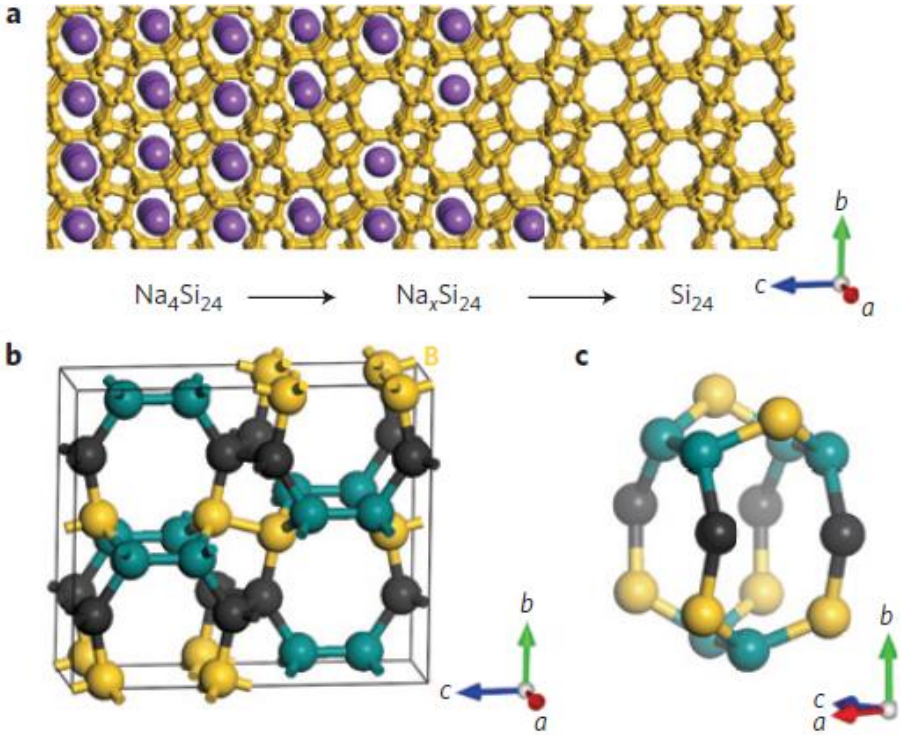
LETTERS

PUBLISHED ONLINE: 17 NOVEMBER 2014 | DOI: 10.1038/NMAT4140

Synthesis of an open-framework allotrope of silicon

Duck Young Kim[1†], Stevce Stefanoski[1†], Oleksandr O. Kurakevych[1,2†] and Timothy A. Strobel[1*†]

Silicon is ubiquitous in contemporary technology. The most stable form of silicon at ambient conditions takes on the structure of diamond (cF8, *d*-Si) and is an indirect bandgap semiconductor, which prevents it from being considered as a next-generation platform for semiconductor technologies[1-4]. Here, we report the formation of a new orthorhombic allotrope of silicon, Si_{24}, using a novel two-step synthesis methodology. First, a Na_4Si_{24} precursor was synthesized at high pressure[5]; second, sodium was removed from the precursor by a thermal 'degassing' process. The *Cmcm* structure of Si_{24}, which has 24 Si atoms per unit cell (oC24), contains open channels along the crystallographic *a*-axis that are formed from six- and eight-membered sp^3 silicon rings. This new allotrope possesses a quasidirect bandgap near 1.3 eV. Our combined experimental/theoretical study expands the known allotropy for element fourteen and the unique high-pressure precursor synthesis methodology demonstrates the potential for new materials with desirable properties.



Si_{136} and Ge_{136} allotropes

On the clathrate form of elemental silicon, Si_{136}: preparation and characterisation of $Na_x Si_{136}$ ($x \rightarrow 0$)

Abdelaziz Ammar [a,1], Christian Cros [a,*], Michel Pouchard [a], Nicolas Jaussaud [a], Jean-Marc Bassat [a], Gérard Villeneuve [b], Mathieu Duttine [b], Michel Ménétrier [a], Edouard Reny [a]

Solid State Sciences 6 (2004) 393–400

Vacuum route

NATURE|Vol 443|21 September 2006 LETTERS

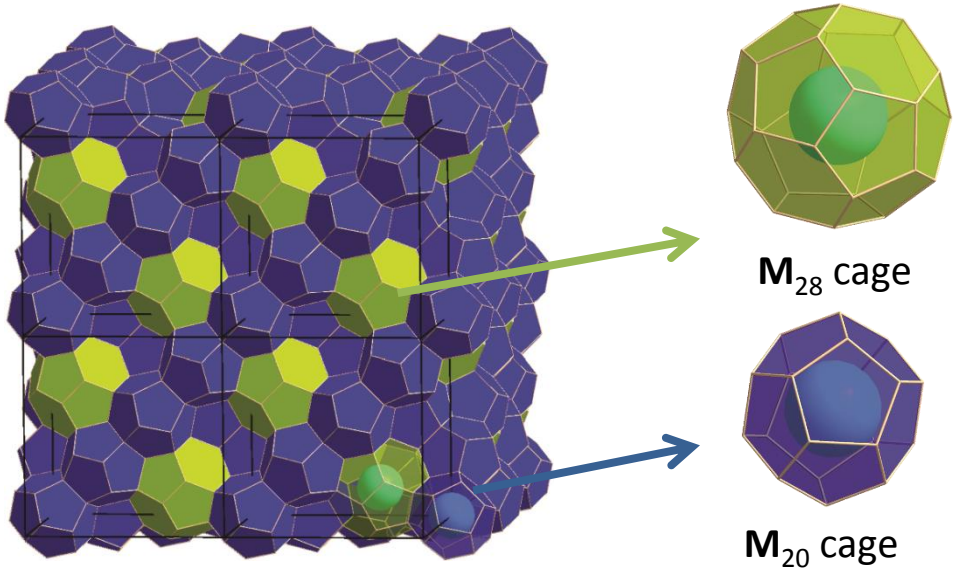
A guest-free germanium clathrate

Ionic liquid route, discussed in a later slide

Arnold M. Guloy[1,2], Reiner Ramlau[1], Zhongjia Tang[1,2], Walter Schnelle[1], Michael Baitinger[1] & Yuri Grin[1]

Clathrate-II (*Fd*-3*m*)

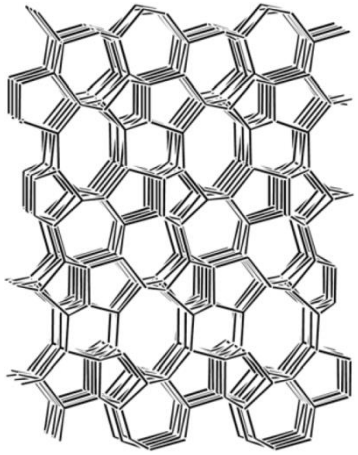
Known for:
Si_{136}
Ge_{136}



(**M** = Si, Ge)
Normally the cages are occupied by guest atoms (Na, K, etc.), but the guests can be removed

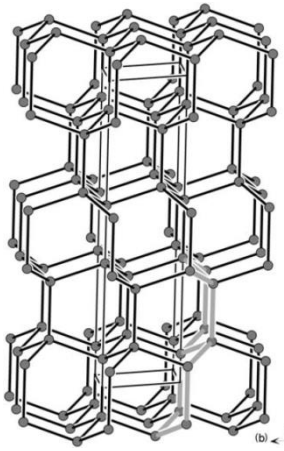
Ge and Sn allotropes

J. Mater. Chem. **2010**, *20*, 1780–1786 (DOI)



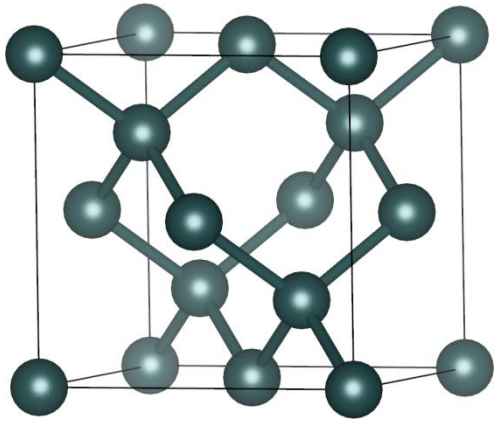
m-allo-Ge

140°C



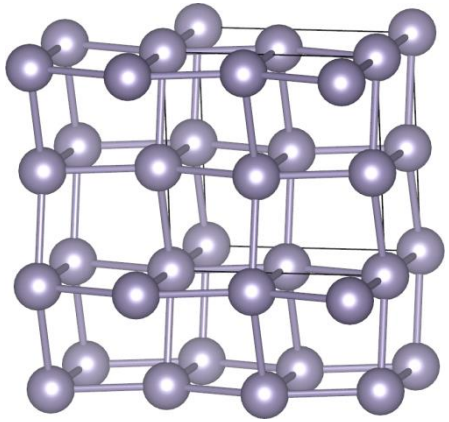
4H-Ge ($P6_3/mmc$)

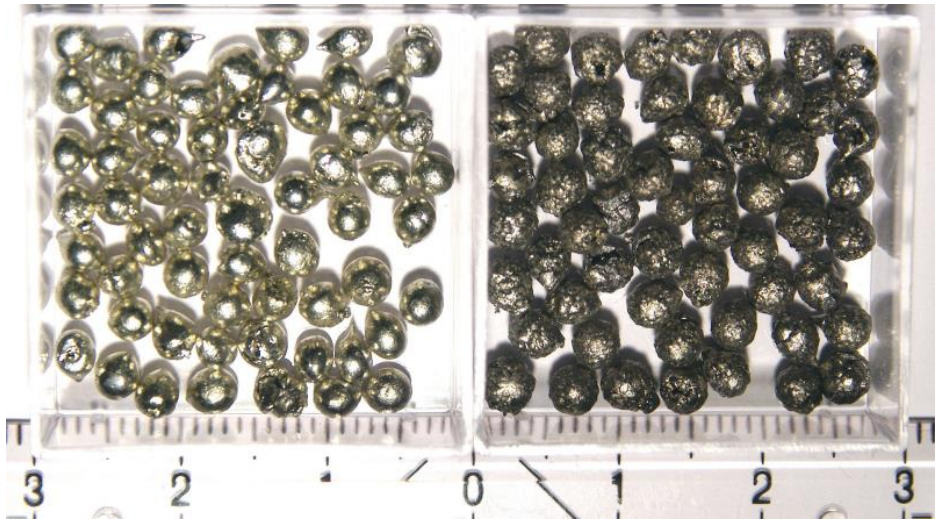
400°C



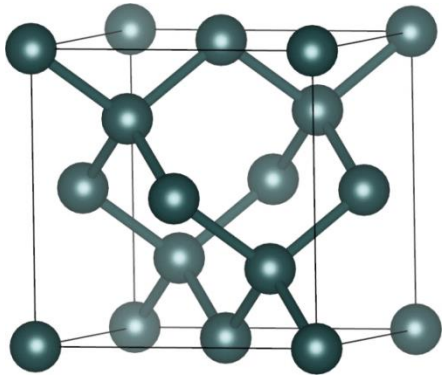
α-Ge (Fd-3m)

β-Sn ($I4_1/amd$)
white tin



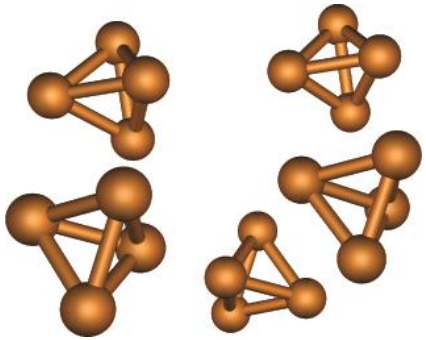


α-Sn (Fd-3m)
grey tin

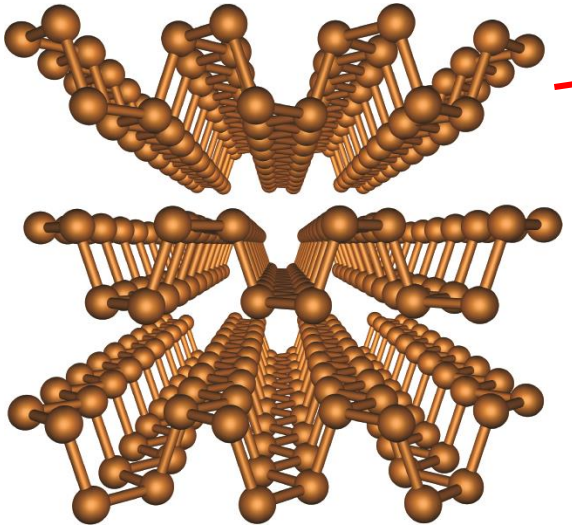


https://crystallography365.wordpress.com/2014/11/23/a-failed-campaign-alpha-and-beta-tin/
https://en.wikipedia.org/wiki/Tin_pest#Napoleon.27s_buttons

Group 15 allotropic modifications

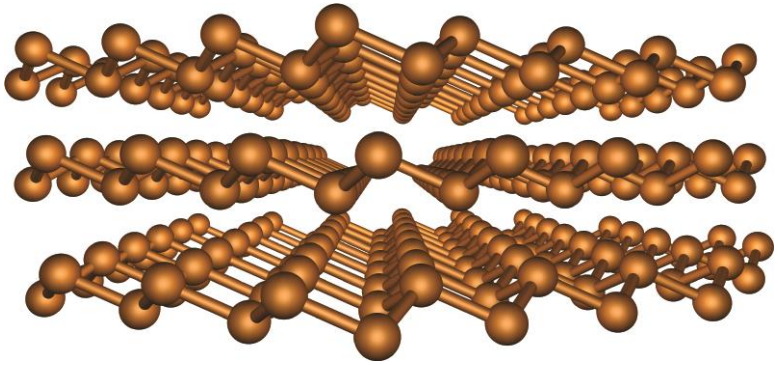


Tetrahedral molecules (P_4, As_4, Sb_4)
White phosphorus

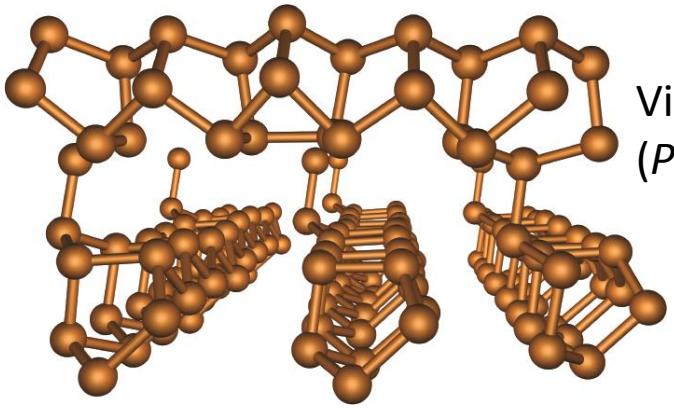


Orthorhombic layered structure, *Cmca* (P, As)
Black phosphorus

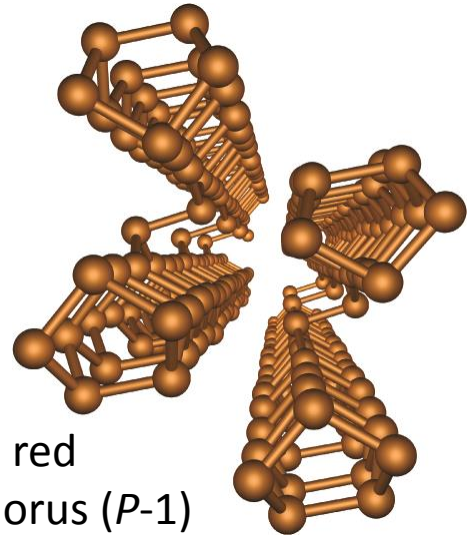
Individual sheets can be cleaved -> phosphorene



Trigonal layered structure, *R*-3*m* (P in high pressure, As, Sb, Bi)



Violet phosphorus (*P*2/*c*)



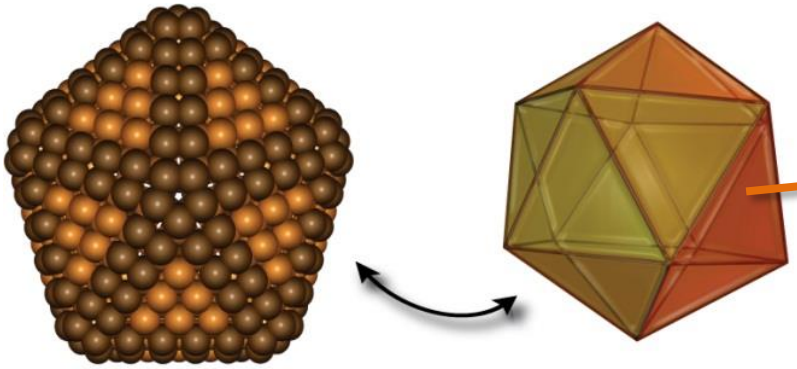
Fibrous red phosphorus (*P*-1)

Figures: AJK

Group 15 nanostructures

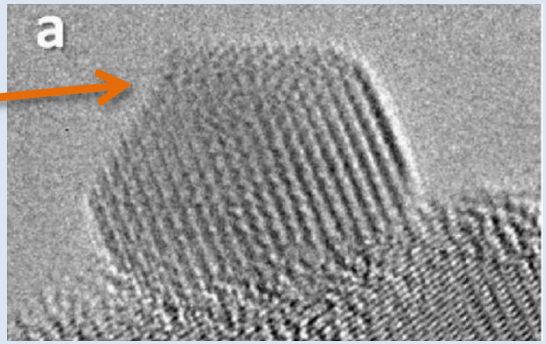
Analogous to the carbon fullerenes and nanotubes, but possess puckered atomic structure

Polyhedra (e.g. P_{180})



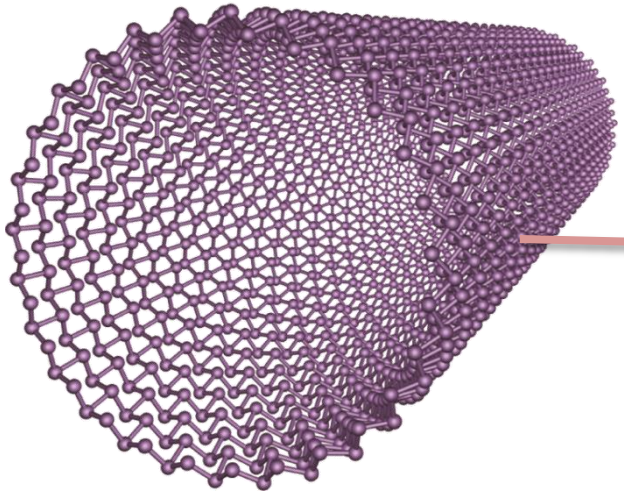
Chem. Eur. J. **2007**, *13,* 5232 (DOI)
Theor. Chem. Acc. **2011**, *129*, 412 (DOI)

Bismuth nanoicosahedra



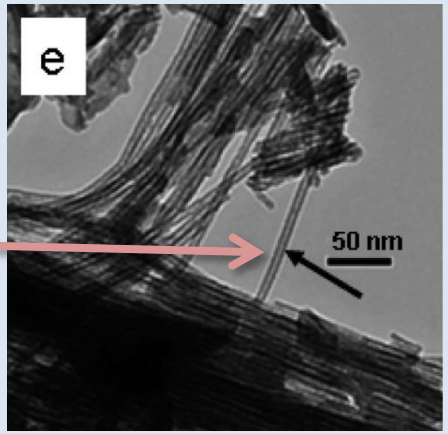
Y. Selzer et al, *Nano Lett.* **2012**, *12,* 1087.

Nanotubes



J. Phys. Chem. C **2009**, 113, 12220 (DOI)

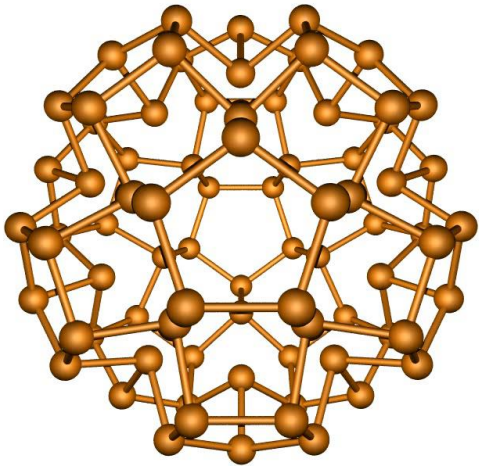
Bismuth nanotubes



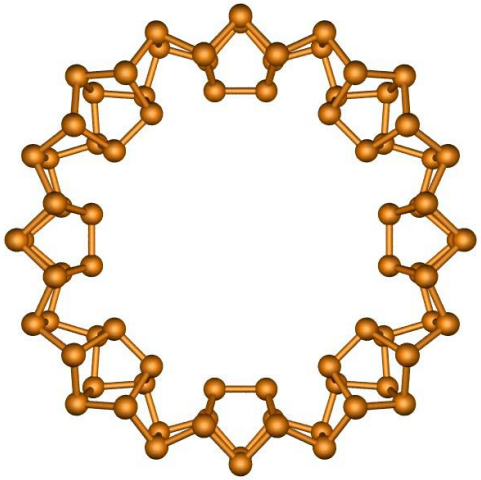
Pfefferle *et al*, *J. Phys. Chem. C*, **2010**, *114*, 3431.

Figures: AJK

Phosphorus nanostructures

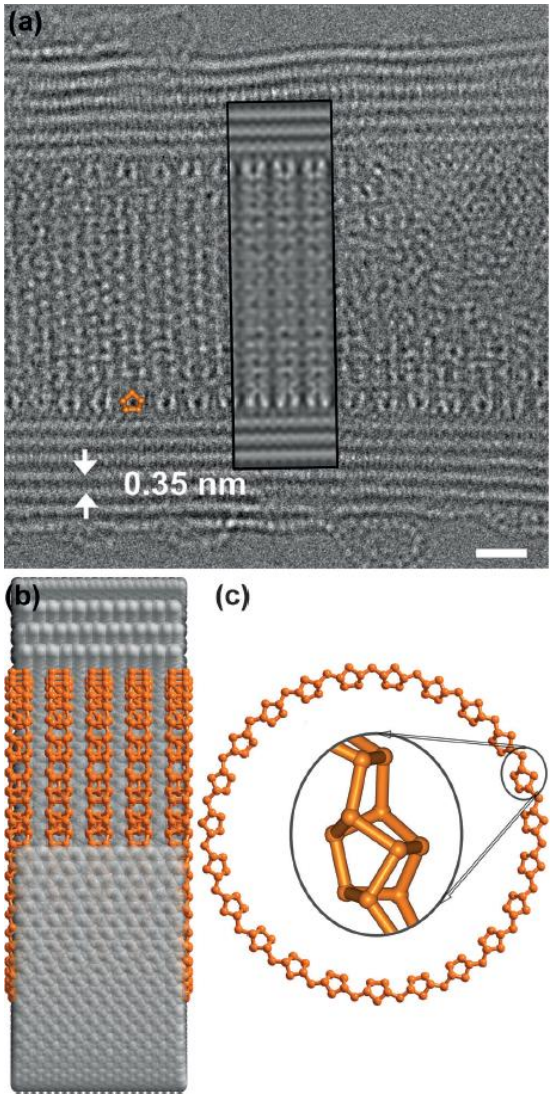


P_{80} fullerene (I_h)

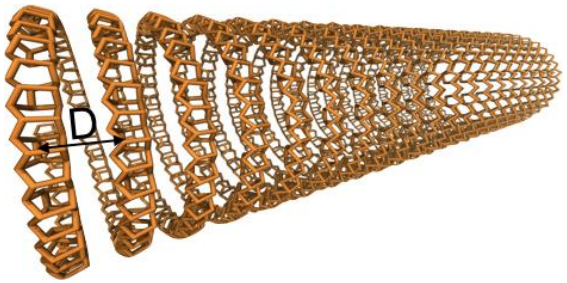


P_{80} ring (C_{4v})

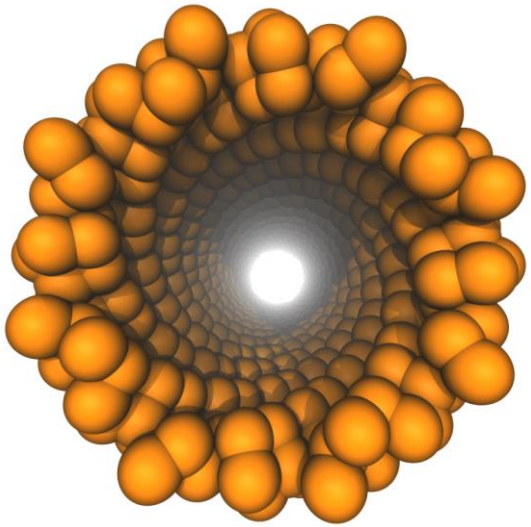
Icosahedral and Ring-shaped Allotropes of Phosphorus
Karttunen, A. J.; Linnolahti, M.; Pakkanen, T. A.
Chem. Eur. J. **2007**, *13*, 5232–5237 (DOI).



Assembly of Ring-Shaped Phosphorus within Carbon Nanotube Nanoreactors, Zhang *et al.*
Angew. Chem. Int. Ed. **2017**, *56*, 1850-1854 (DOI).



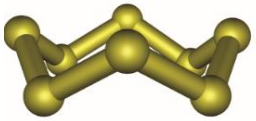
Red phosphorus helices



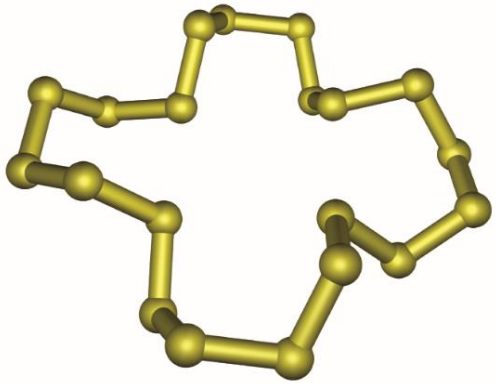
One-dimensional Phosphorus Nanostructures: from Nanorings to Nanohelices
Sansone, G.; Maschio, L.; Karttunen, A. J. *Chem. Eur. J.* **2017**, *23*, 15884–15888. (DOI).

Group 16 allotropes

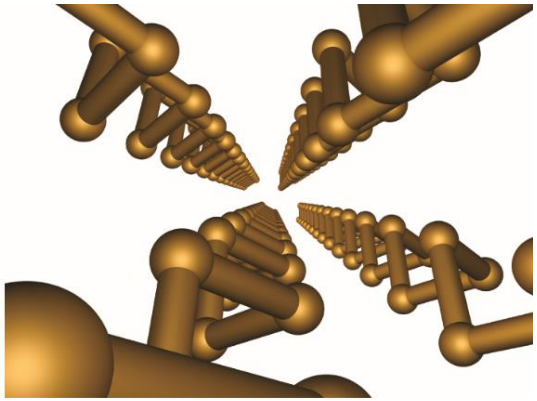
- Whereas the allotropes of group 15 elements are three-coordinate, the additional valence electron of group 16 elements makes their allotropes two-coordinate
- While this imposes some limits on their capability to form infinite structural networks, the elemental chemistry of sulfur and selenium is very rich due to their abilities to catenate in various ways
- The only known crystalline form of tellurium at room pressure is similar to gray selenium



α-cyclo-S_8 (*Fddd*)



Cyclo-S_{20} (*Pbcn*)



Gray selenium consisting of helical chains ($P3_121$)

Figures: AJK

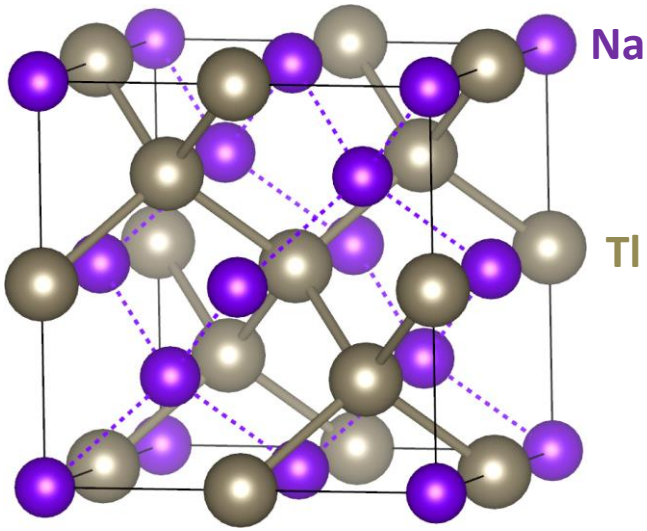
Zintl phases

- Zintl phases are ***valence-balanced*** semiconductors
  - Charge transfer from Group 1 or 2 elements to Group 13-16 elements
- For example, NaTl (sodium thallide)
  - Each Na atom donates $1e^-$
  - Each Tl atom accepts $1e^-$
- The electron configuration of the anionic Tl network is now **analogous to group 14 elements**
  - Tl atoms adopt 4-coordinated diamond structure
  - The Na^+ ions are packed as diamond, too
  - Covalent bonding within the Tl network, ionic bonding between the anionic network and the cations (or mixed ionic / covalent)
- Basically, ***the 8-electron rule*** in action
- Ideally, Zintl phases should be **semiconducting**
  - However, in reality many are metallic (e.g. NaTl)
  - Bonding is more complex than the ideal ”valence-balanced” (or there are impurities)

Periodic table of electronegativity by Pauling scale

1	2	13	14	15	16	17
H 2.20						
Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66
Cs 0.79	Ba 0.89	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Uut	Fl	Uup	Lv	Uus

Figure: Wikipedia/AJK



NaTl (*Fd*-3*m*)

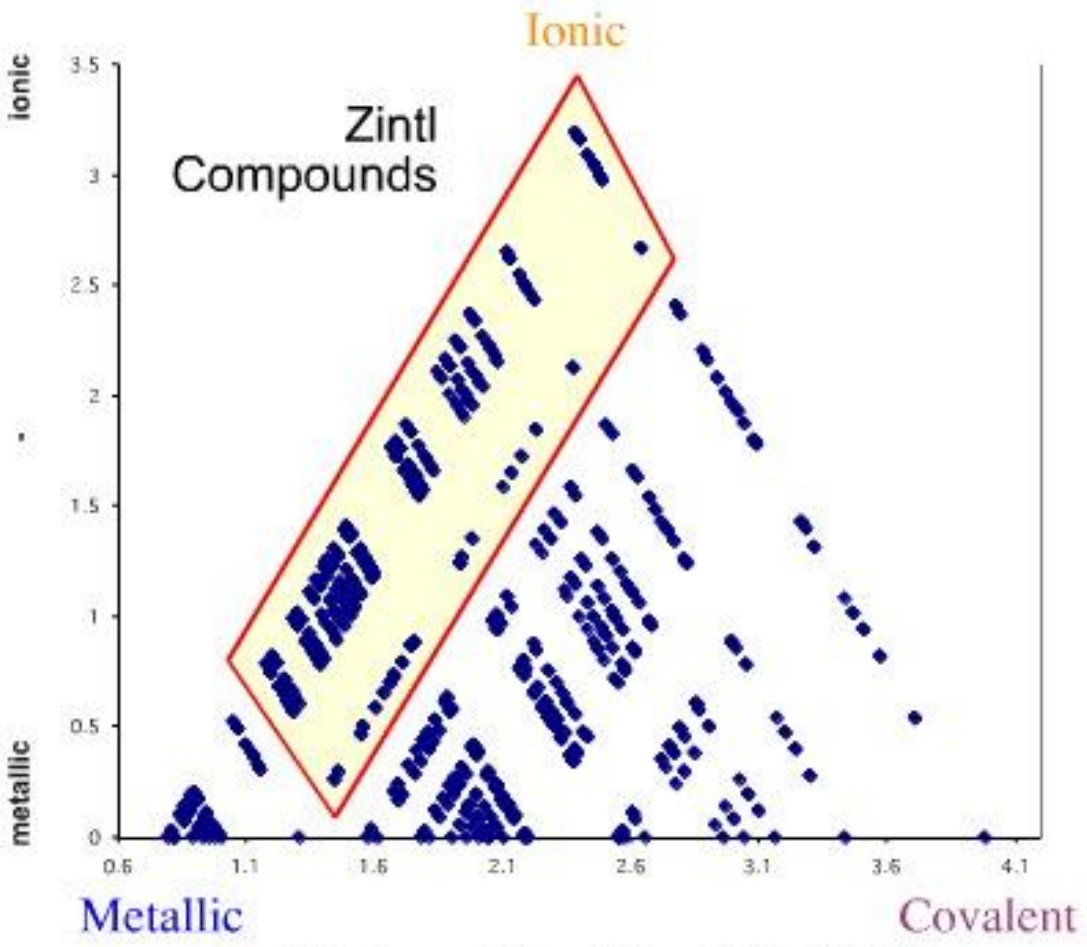
Figure: AJK

Zintl phases and electronegativity

Revised Pauling Electronegativity Difference

$$\Delta\chi = |\chi_a - \chi_b|$$

van Arkel-Ketalaar Triangle



after W.B. Jensen *J.Chem.Educ.* (1995), **72**, 395)

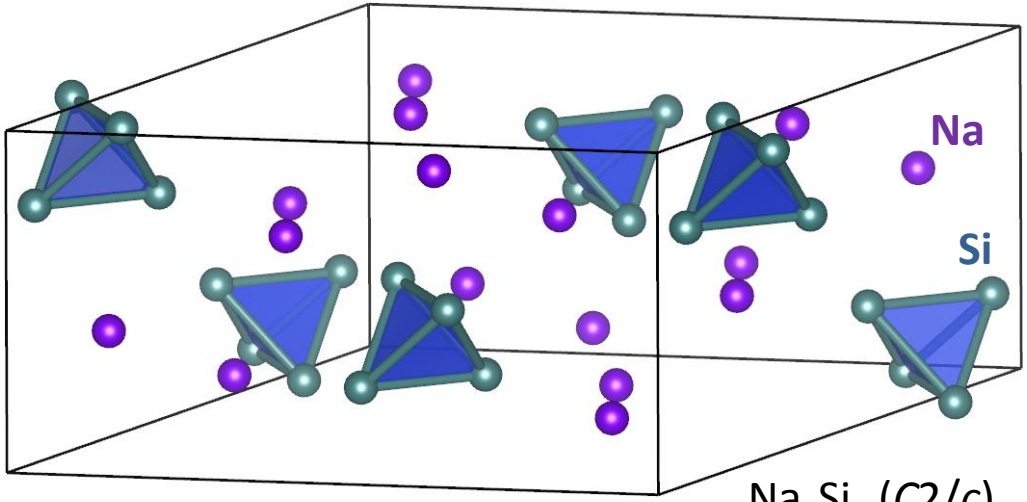
Average Revised Pauling Electronegativity

$$\Sigma\chi = \frac{(\chi_a + \chi_b)}{2}$$

Figure: http://www.meta-synthesis.com/webbook/37_ak/triangles.html

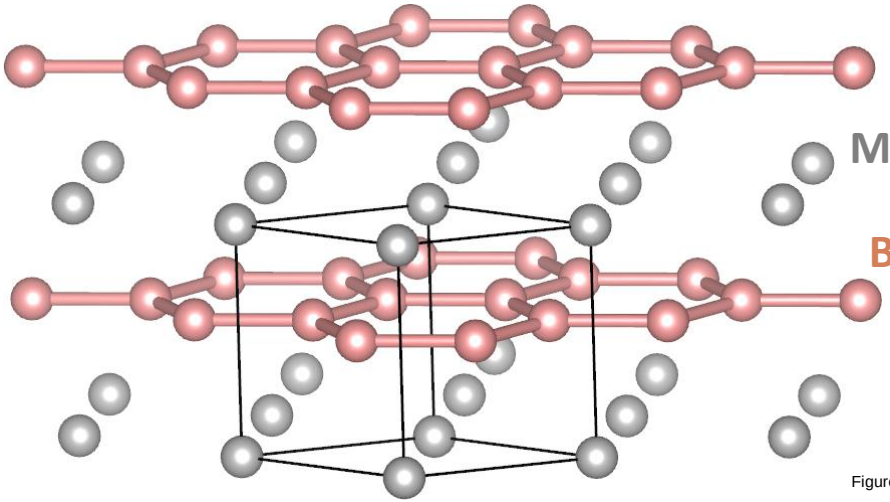
Examples of Zintl phases (1)

- **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 (*C*2/*c*)

- **MgB_2**
- Each Mg atom donates 2e^-
- Each B atom accepts 1e^-
- The resulting two-dimensional B-network is isoelectronic with graphene

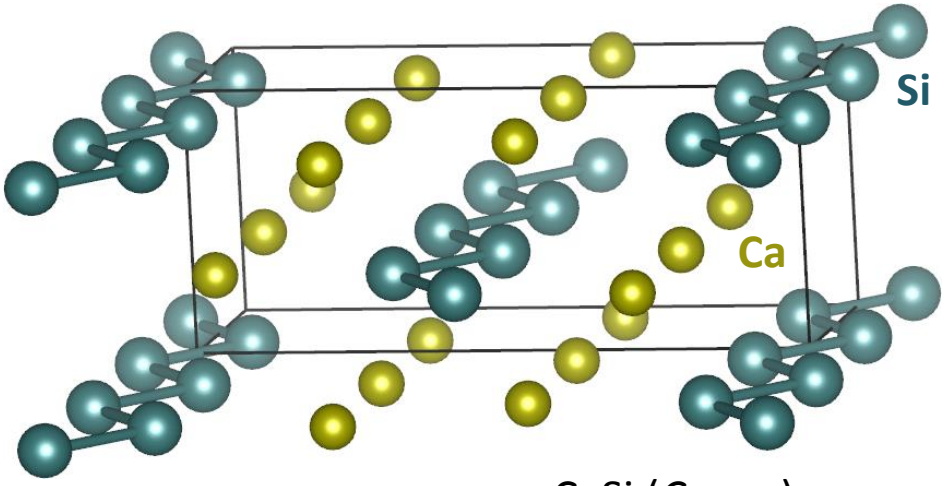


Figures: AJK

MgB_2 (*P*6/*mmm*)

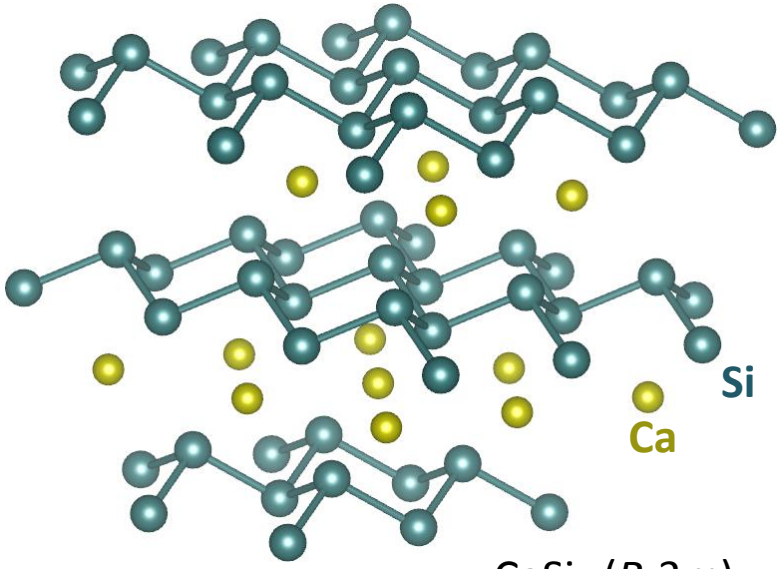
Examples of Zintl phases (2)

- **CaSi**
- Each Ca atom donates $2e^-$
- Each Si atom accepts $2e^-$
- The resulting one-dimensional Si-chains are closely related to Se-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*)

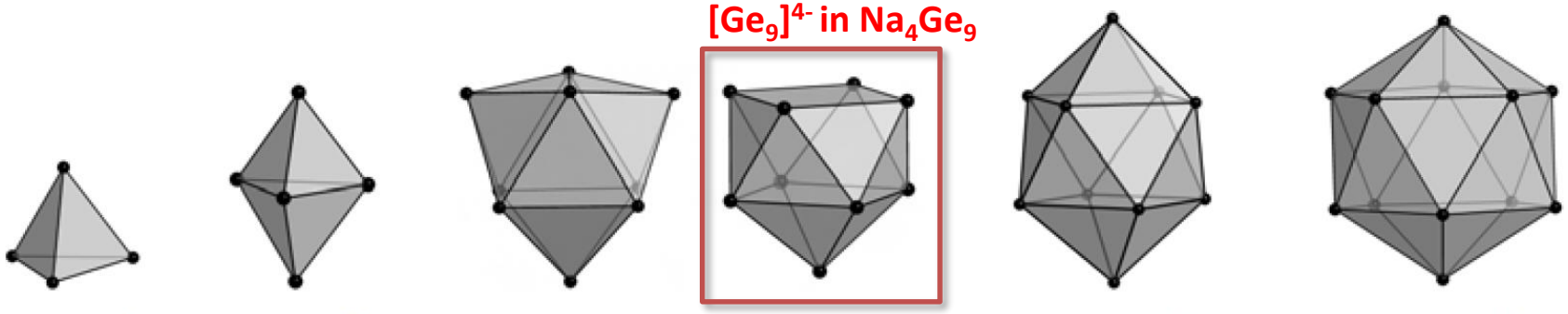
Figures: AJK

Group 14 Zintl ions (Si, Ge, Sn, Pb)

Many solid-state Zintl phases contain discrete anions

For example, $[Ge_9]^{4-}$ in Na_4Ge_9

Figure: Sandra Scharfe / Dissertation 2010 (TUM)



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

$[Si_4]^{4-}$ in Na_4Si_4

Strained bond angles in comparison to diamond-like bulk α-Si / α-Ge / α-Sn with 109.5° angles

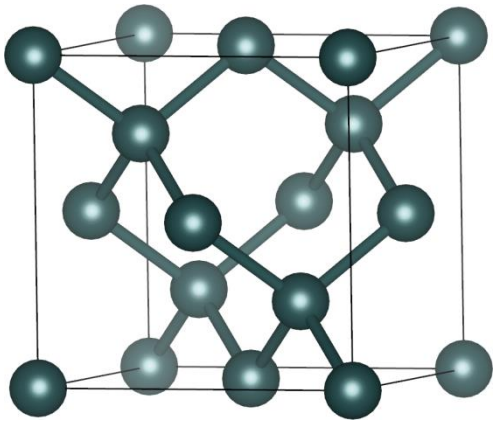
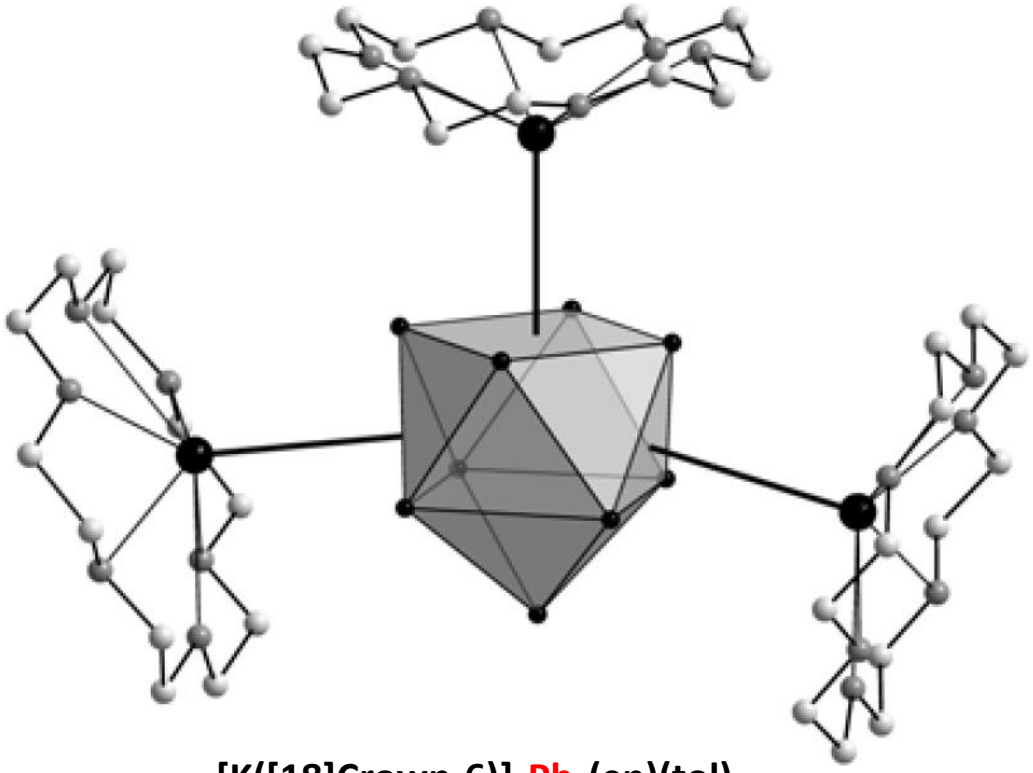


Figure: AJK

Zintl ions can be crystallized from solution



[K([18]Crown-6)]$_4$Pb$_9$(en)(tol)

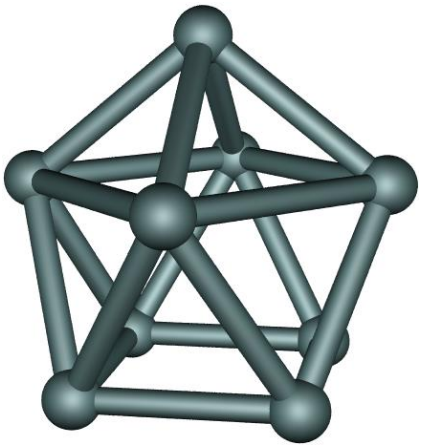
S. Scharfe, Dissertation, Technical University of Munich, **2010**

Zintl phases as precursors for preparing novel materials

NATURE|Vol 443|21 September 2006 LETTERS

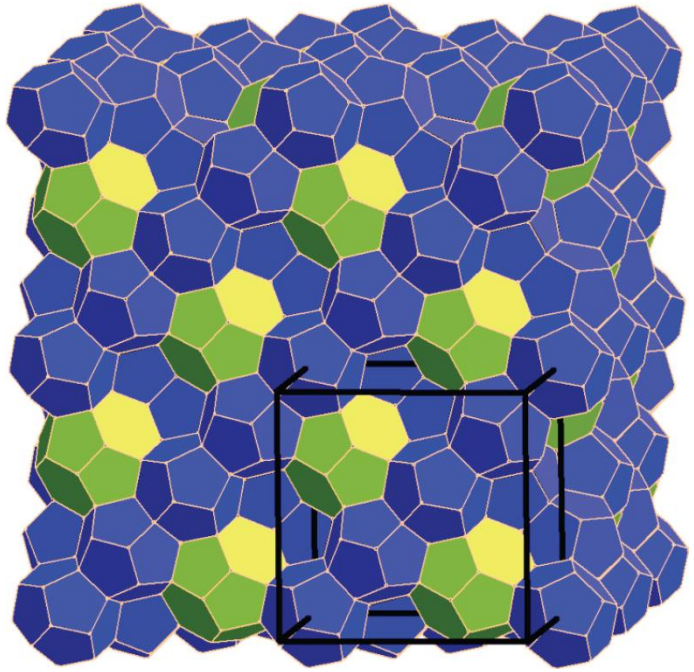
A guest-free germanium clathrate

Arnold M. Guloy[1,2], Reiner Ramlau[1], Zhongjia Tang[1,2], Walter Schnelle[1], Michael Baitinger[1] & Yuri Grin[1]



$[Ge_9]^{4-}$ (in Na_4Ge_9)

Mild oxidation in ionic liquid

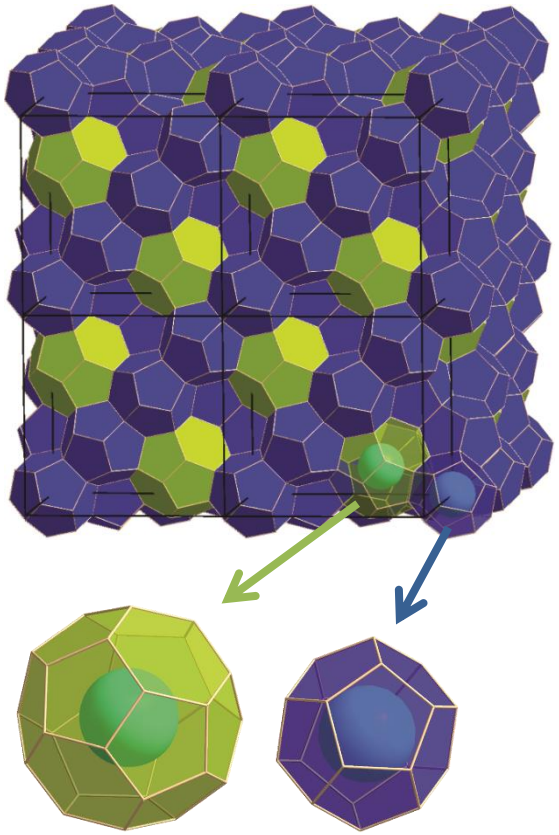


Ge_{136} Clathrate-II (*cF*136)

Zintl phases: Semiconducting group 14 clathrates (1)

- The microporous 3D framework of the group 14 clathrates is composed of fused atomic cages
- The cages are normally occupied by guest atoms, but guest-free Si- and Ge-frameworks are known, as well
- The group 14 clathrates are excellent thermoelectric materials[1]
  - Great thermal properties
  - Good electronic properties

Clathrate-II (*Fd*-3*m*)



$\mathbf{M}_{28}$ cage $\mathbf{M}_{20}$ cage

(**M** = Si, Ge, Sn)

[1] G. S. Nolas et al. *Phys. Rev. Lett.*, **1999**, *82*, 779.
G. S. Nolas et al. *J. Mater. Chem.*, **2008**, *18*, 842.
B. B. Iversen et al. *Dalton Trans.*, **2010**, *39*, 978.

Zintl phases: Semiconducting group 14 clathrates (2)

- Charge transfer occurs between the guest and the framework
- The charge is (usually) balanced by heteroatoms in the framework
  - Metallic systems such as $Na_{24}Si_{136}$ are also known
- **The atomic composition and properties can be tuned rather accurately!**

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

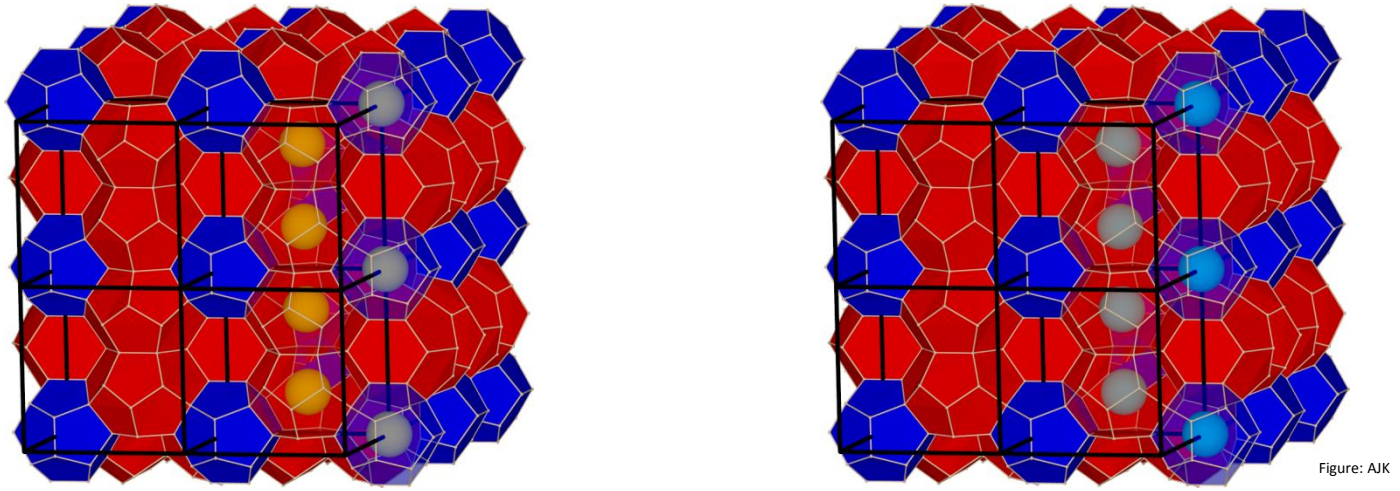


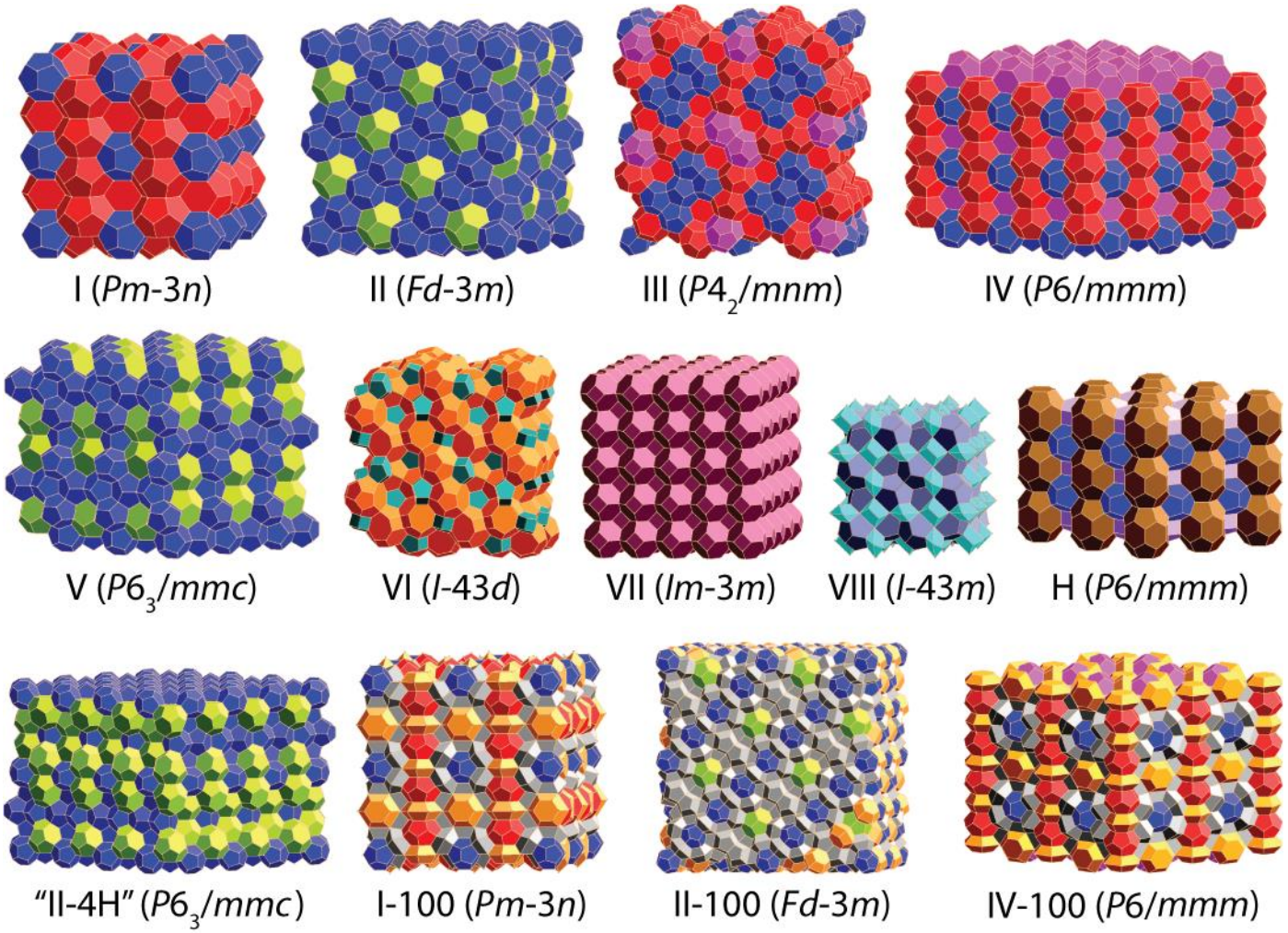
Figure: AJK

- $Ba_8[Ga_{16}Ge_{30}]$ (**anionic** framework)
- Each Ba atom donates $2e^-$
- Ga atoms have $1e^-$ less than Ge, so the 4-coordinated framework needs $16e^-$

- $I_8[As_8Ge_{38}]$ (**cationic** framework!)
- Each I atom accepts $1e^-$
- As atoms have $1e^-$ more than Ge, these extra electrons are donated to the I atoms

Examples of clathrate frameworks

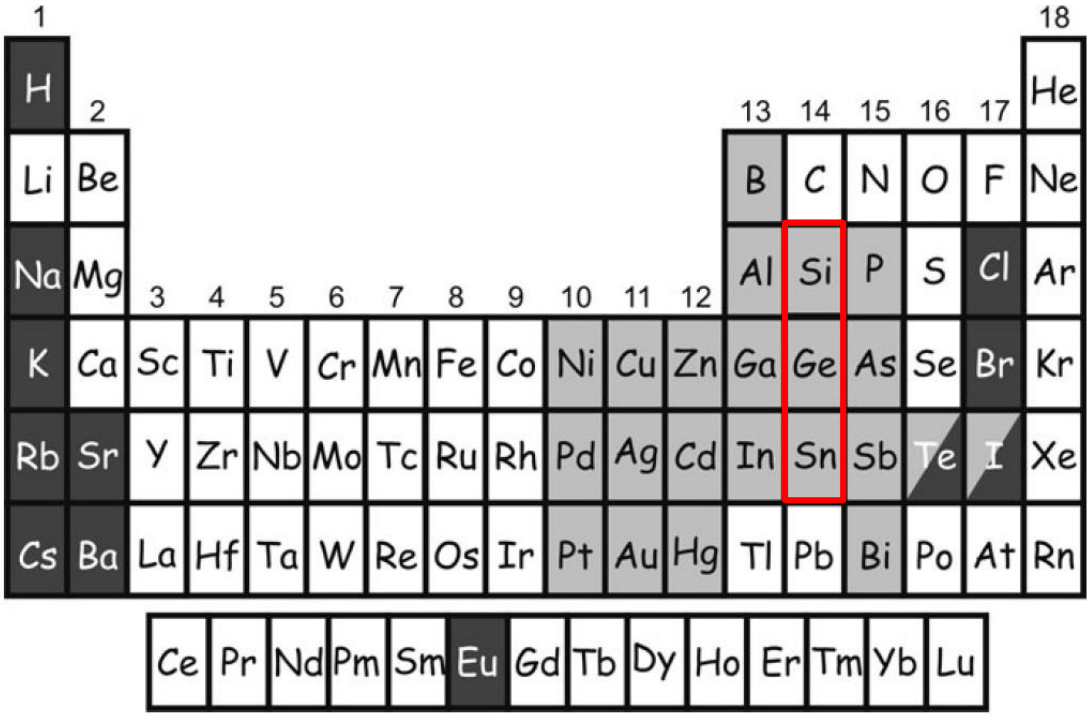
Very rich structural chemistry (all frameworks are not yet known for group 14 clathrates)



A. J. Karttunen, T. F. Fässler, M. Linnolahti, T. A. Pakkanen *Inorg. Chem.* **2011**, *50*, 1733.

Currently known group 14 clathrates

Guest atoms



Framework atoms

200+ phases are currently known. Typical synthesis routes:

- Shake & Bake
- Flux method
- Czochralski pulling

Shevelkov, A. V.; Kovnir, K. *Struct. Bond.* **2011**, *139*, 97.

Recent review: Dolyniuk, J.-A.; Owens-Baird, B.; Wang, J.; Zaikina, J. V.; Kovnir K. *Materials Science and Engineering*, **2016**, *R108*, 1–46

Examples of clathrate phases

Si-based	Ge-based	Ge-based	Sn-based
$Na_8[Si_{46}]$	$K_8[Al_8Ge_{38}]$	$I_8[Ge_{38}P_8]$	$K_{1.6}Cs_{6.4}[Sn_{44}\square_2]$
$Na_{8-x}Ba_x[Si_{46}]$	$Rb_8[Al_8Ge_{38}]$	$Br_8[Ge_{38}P_8]$	$Rb_8[Sn_{44.6}\square_{1.4}]$
$Na_xBa_6[Si_{46}]$	$K_8[Ga_8Ge_{38}]$	$Cl_8[Ge_{38}P_8]$	$Cs_8[Sn_{44}\square_2]$
$K_{7.62}\square_{0.38}[Si_{46}]$	$Rb_8[Ga_8Ge_{38}]$	$I_8[Ge_{38}As_8]$	$K_8[Al_8Sn_{38}]$
$Rb_{6.15}\square_{1.85}[Si_{46}]$	$Cs_8[Ga_8Ge_{38}]$	$Br_8[Ge_{38}As_8]$	$Rb_8[Al_8Sn_{38}]$
$K_8[Ga_8Si_{38}]$	$K_8[In_8Ge_{38}]$	$Cl_8[Ge_{38}As_8]$	$K_8[Ga_8Sn_{38}]$
$Rb_8[Al_8Si_{38}]$	$Rb_8[In_8Ge_{38}]$	$I_8[Ge_{38}Sb_8]$	$Rb_8[Ga_8Sn_{38}]$
$Rb_8[Ga_8Si_{38}]$	$Cs_8[In_8Ge_{38}]$	$Br_8[Ge_{38}Sb_8]$	$Cs_8[Ga_8Sn_{38}]$
		$I_8[Ge_{14}Ga_{12}Sb_{20}]$	$Cs_8[Zn_4Sn_{42}]$
			$Cs_8[Cd_4Sn_{42}]$

Kovnir, K.; Shevelkov, A. V. *Russ. Chem. Rev.* **2004**, *73*, 923.

Extra slides: Li_3NaGe_2

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

Angew. Chem. Int. Ed. **2016**, *55*, 1075–1079 (DOI).

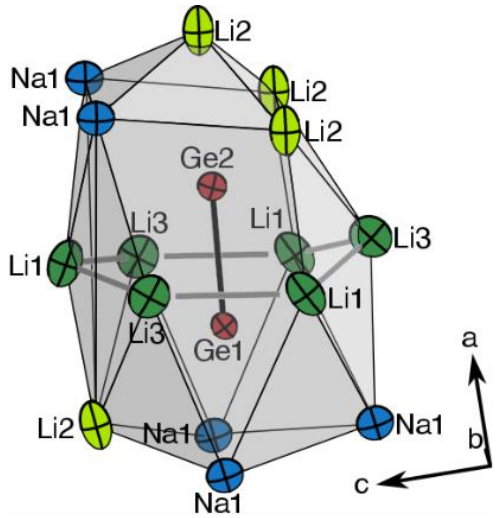
Angewandte International Edition Chemie

VIP Zintl Phases Very Important Paper

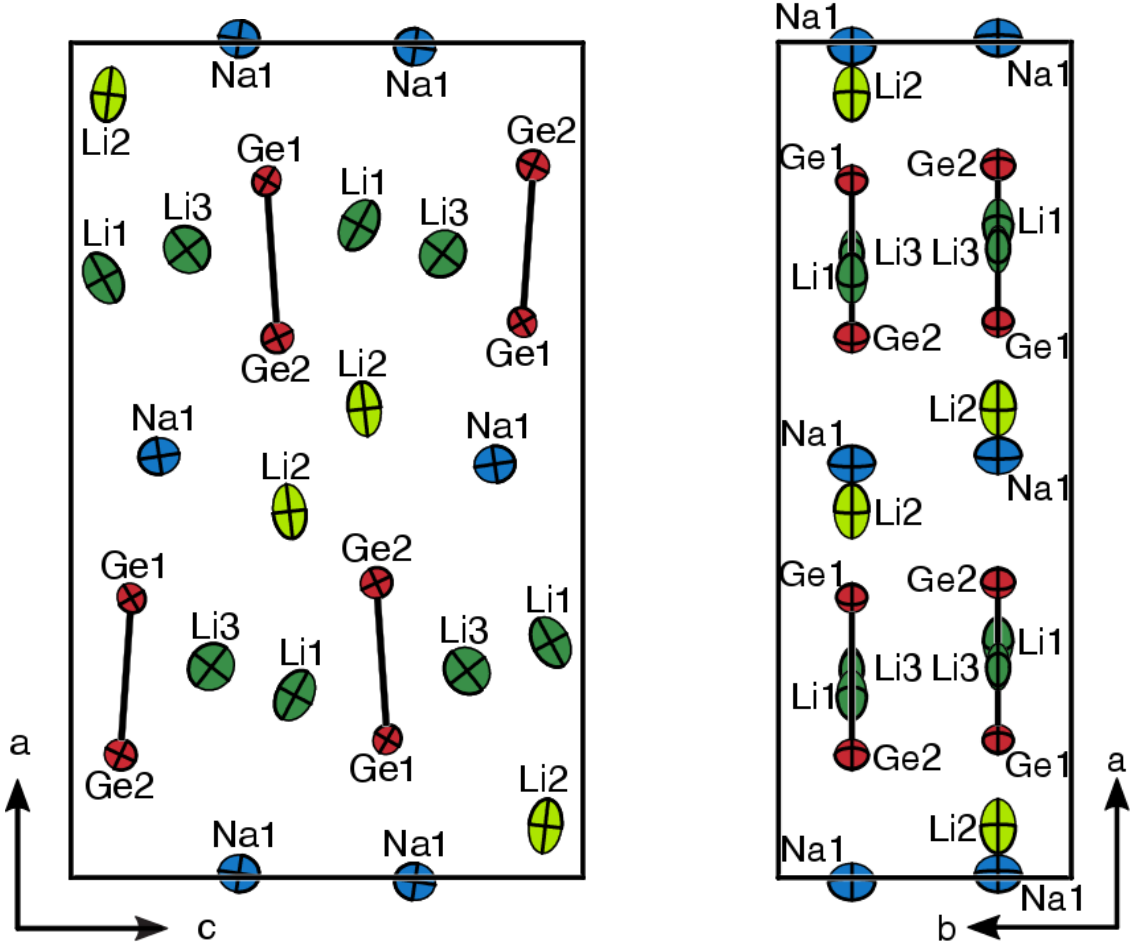
International Edition: DOI: 10.1002/anie.201508044
German Edition: DOI: 10.1002/ange.201508044

$[Ge_2]^{4-}$ Dumbbells with Very Short Ge–Ge Distances in the Zintl Phase Li_3NaGe_2: A Solid-State Equivalent to Molecular O_2

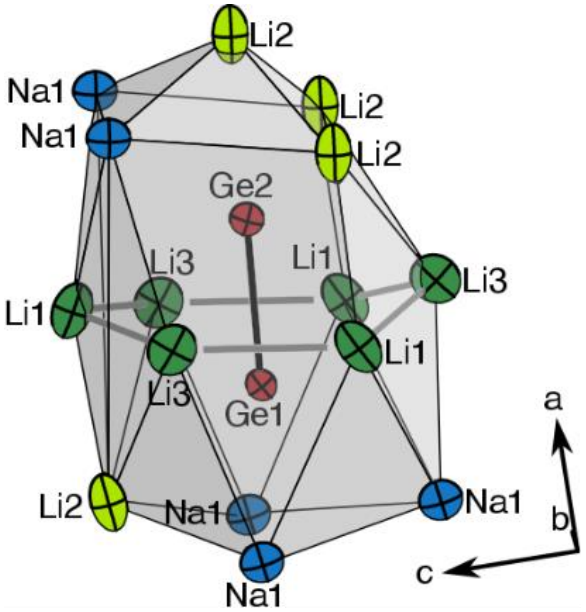
*Lavinia M. Scherf, Antti J. Karttunen, Oliver Pecher, Pieter C. M. M. Magusin, Clare P. Grey, and Thomas F. Fässler**

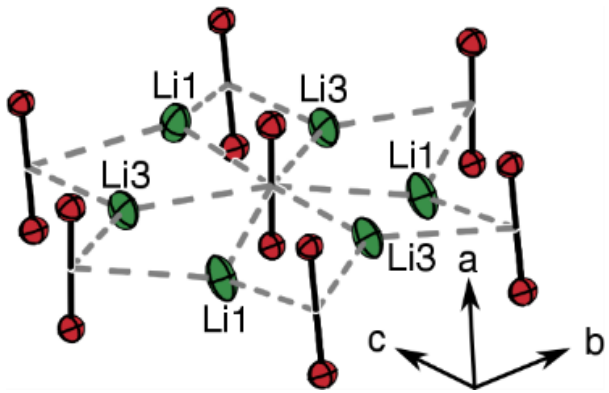


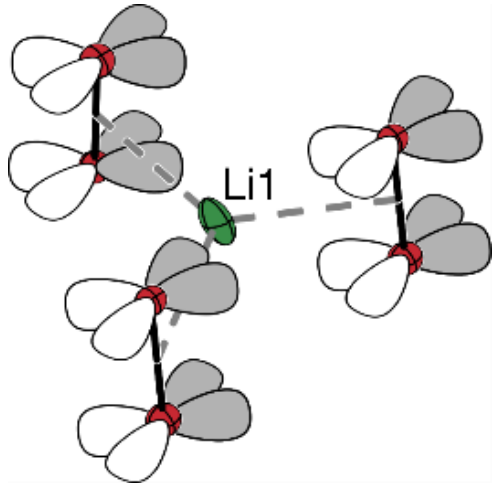
Li_3NaGe_2 phase: $(Li^+)_3(Na^+)[Ge_2]^{4-}$?



Coordination sphere of $[Ge_2]^{4-}$

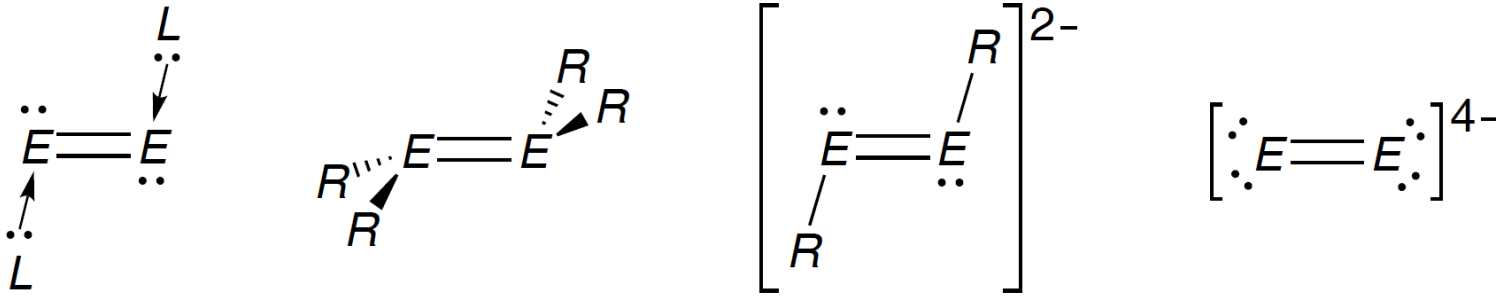






Li1 and Li3 coordinate to the π-system of $[Ge_2]^{4-}$?

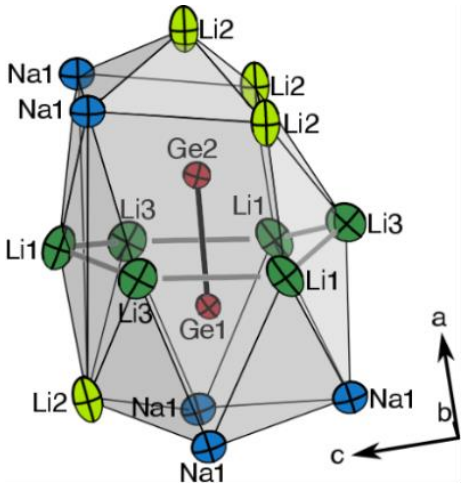
Bond lengths in double-bonded Si and Ge compounds



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])

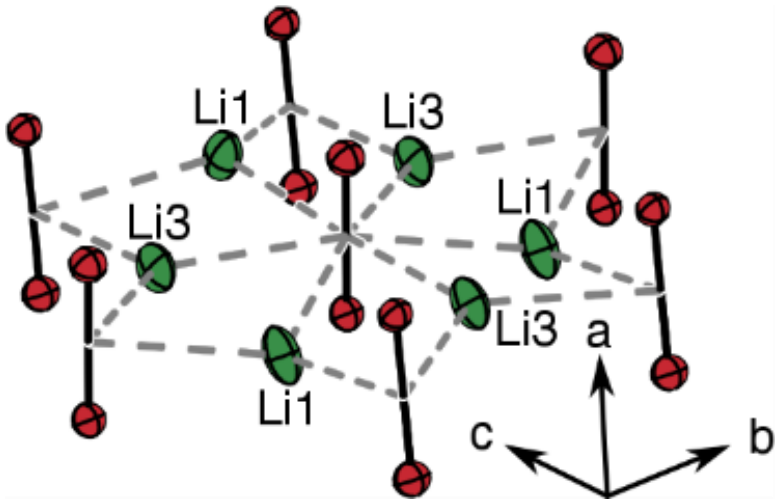
$[Ge_2]^{4-}$ bond distance in Li_3NaGe_2: 2.390(1) Å

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

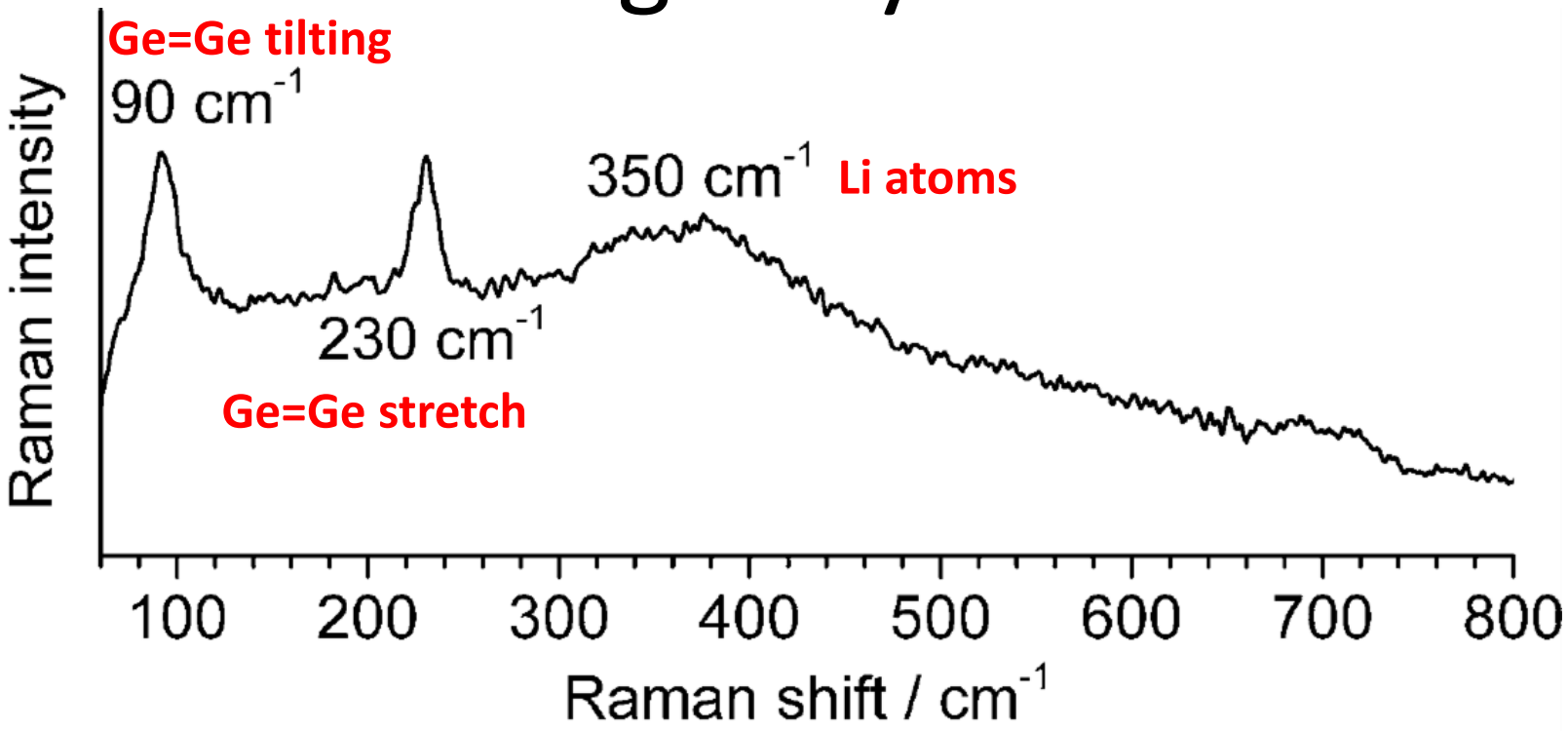


Characterization of the $[Ge_2]^{4-}$ double-bond

- Raman spectroscopy (Ge=Ge stretch?)
- NMR spectroscopy (^{6}Li chemical shifts for Li1/Li3)
- Quantum chemical calculations (DFT)
  - Band structure / molecular orbitals
  - Interpretation of Raman and NMR spectra

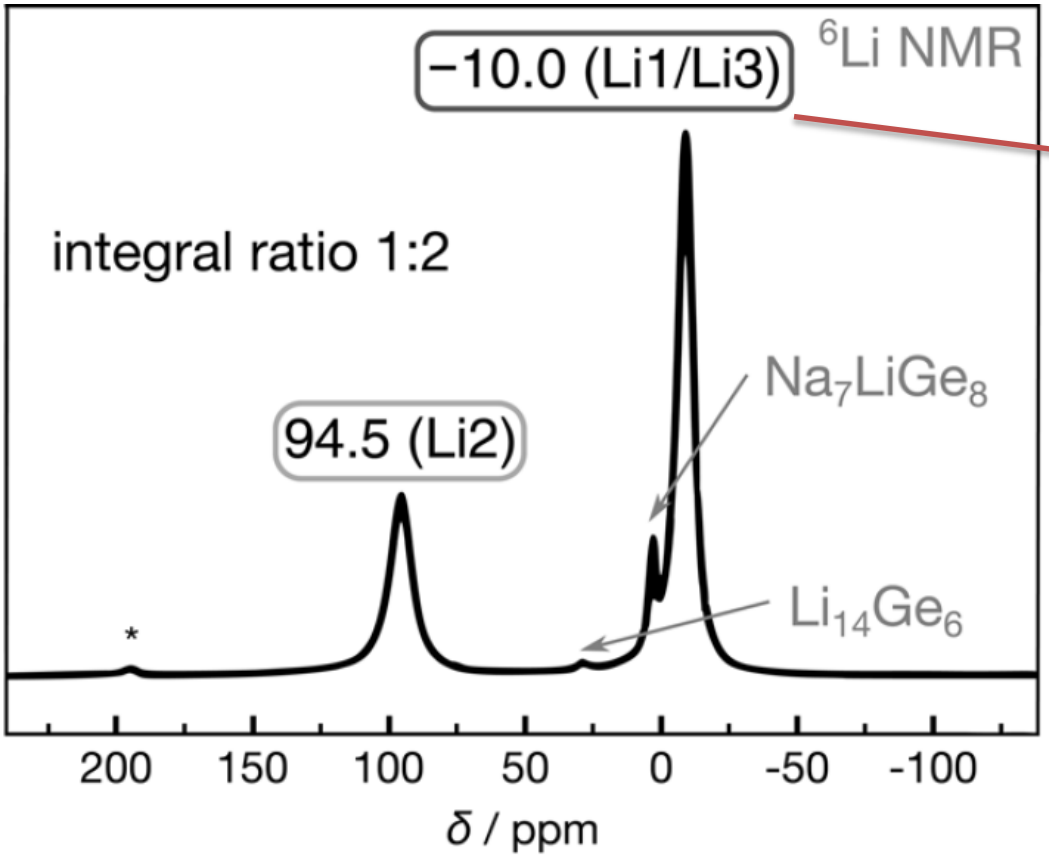


Raman spectrum of a Li_3NaGe_2 single crystal

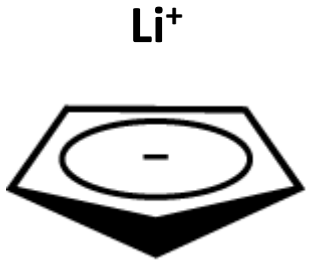


Assignment of the modes: Quantum chemical calculations (DFT-PBE0/TZVP)

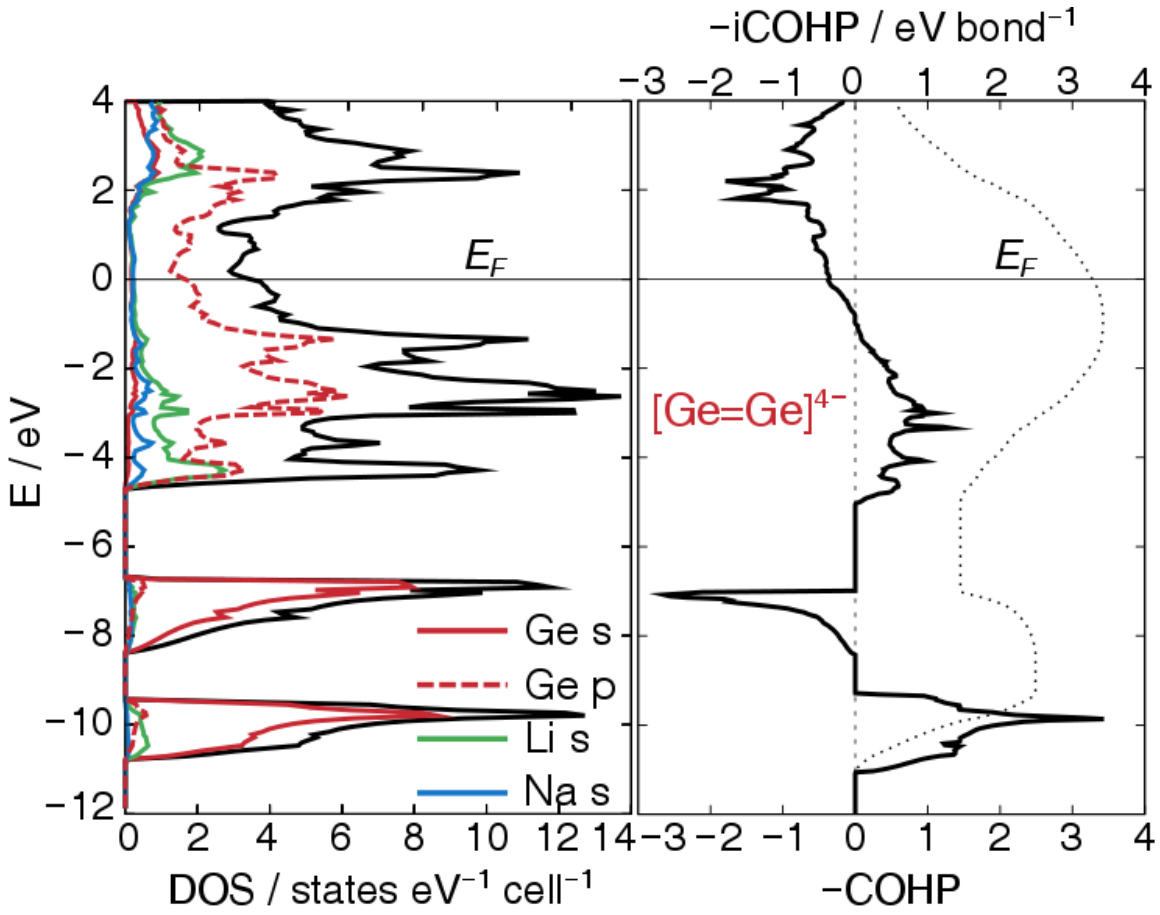
^{6}Li NMR on Li_3NaGe_2 (+ quantum chemical calculations)



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



According to band structure analysis, Li_3NaGe_2 is metallic

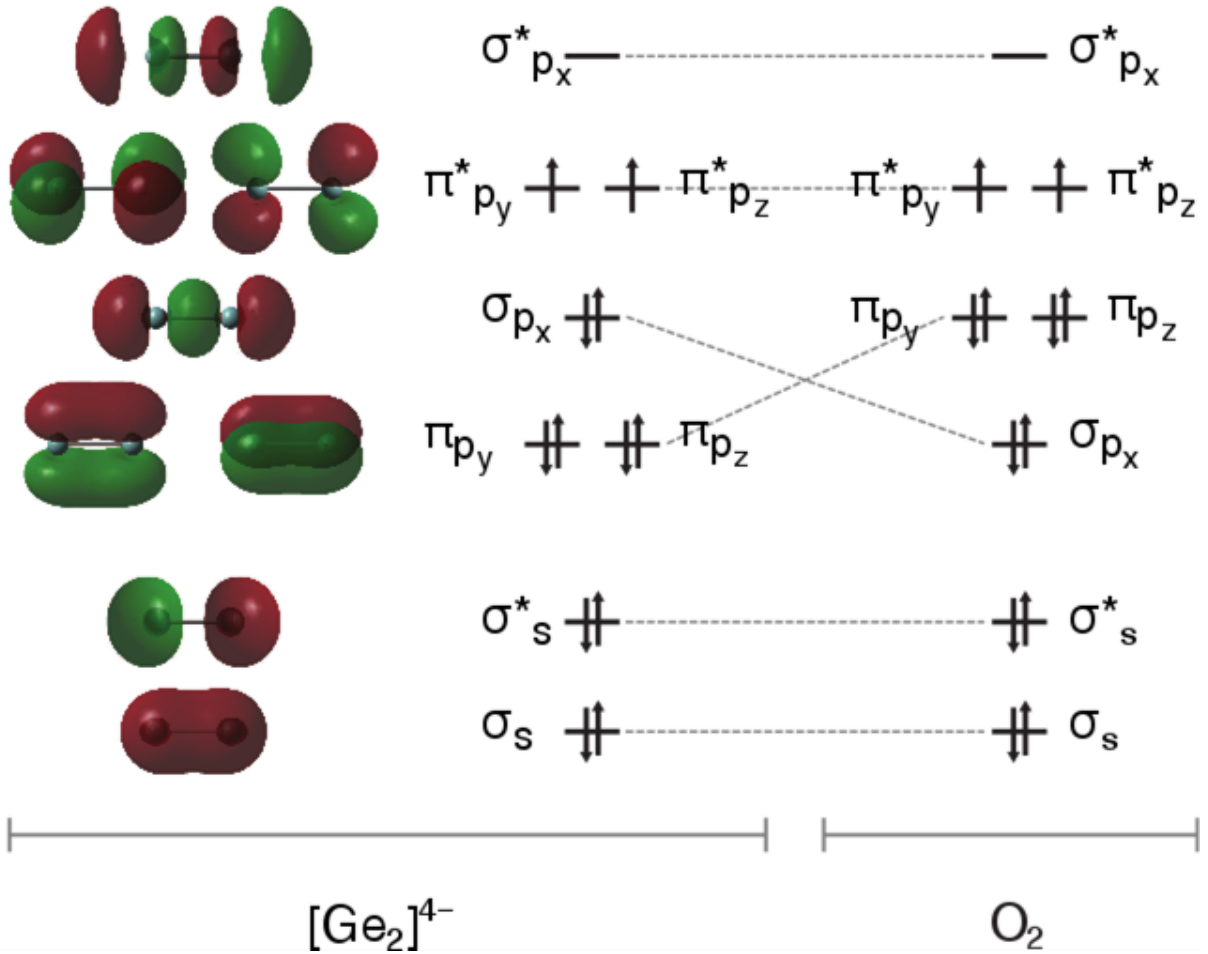


Unoccupied bands

Fermi level

Occupied bands

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



Unpaired electrons

-> partially occupied bands

-> metallic (conducting) solid

Summary

- Li_3NaGe_2 shows the shortest Ge–Ge distance ever observed in a Zintl phase
- Raman data, NMR data, together with quantum chemical calculations, strongly support the idea of double-bonded $[Ge_2]^{4-}$
- Band structure and molecular orbital analyses show that the ligand-free $[Ge_2]^{4-}$ is in fact a **solid-state equivalent to O_2**