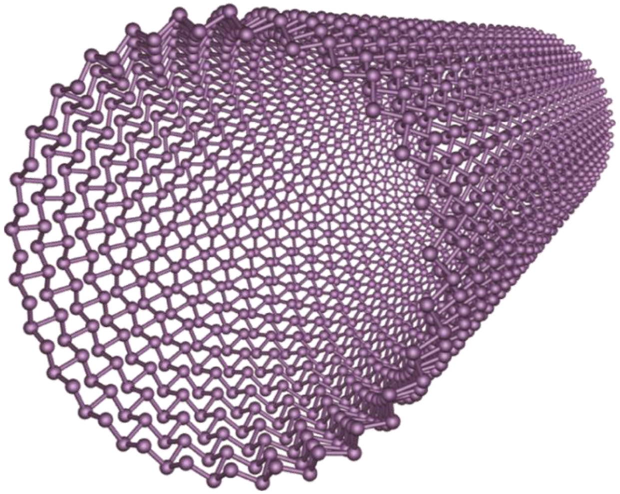
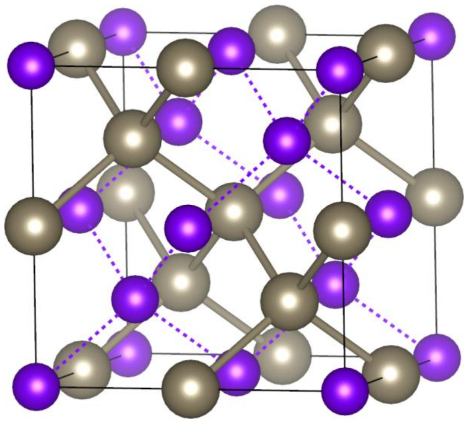
Lecture 10:
Main group compounds

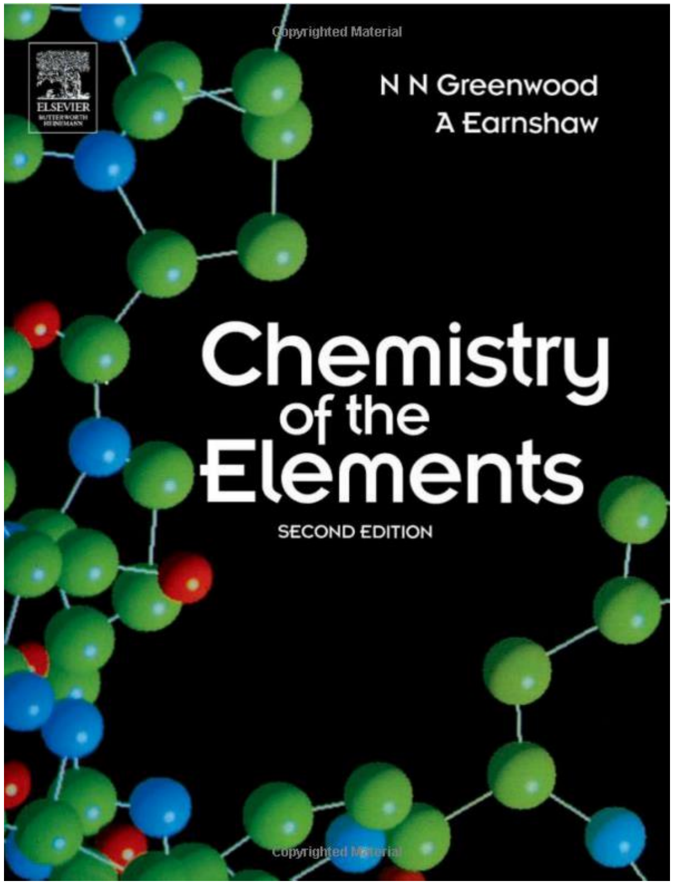
- Some general trends and classifications for non-molecular main group compounds
- Allotropes
  - Group 14 elements
  - Group 15 elements
  - Group 16 elements
- Zintl phases
  - General principles
  - Typical examples
  - Zintl ions
  - Semiconducting clathrates





Figures: AJK

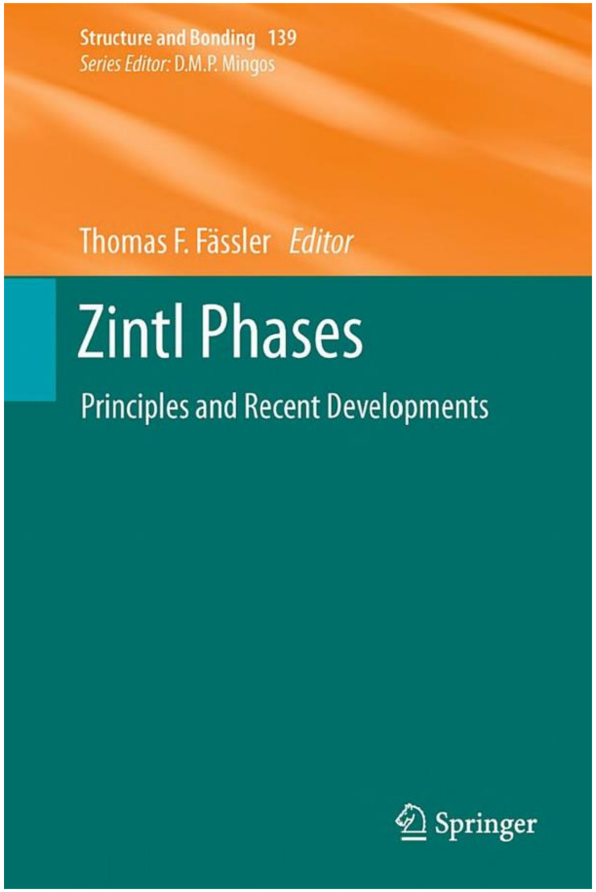
Literature



N N Greenwood
A Earnshaw

Chemistry of the Elements

SECOND EDITION



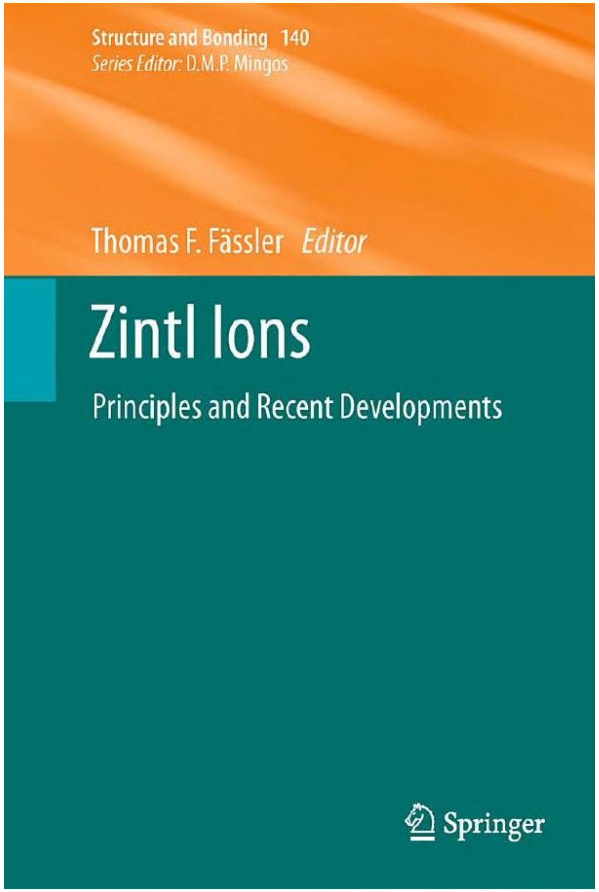
Structure and Bonding 139
Series Editor: D.M.P. Mingos

Thomas F. Fässler *Editor*

Zintl Phases

Principles and Recent Developments

Springer



Structure and Bonding 140
Series Editor: D.M.P. Mingos

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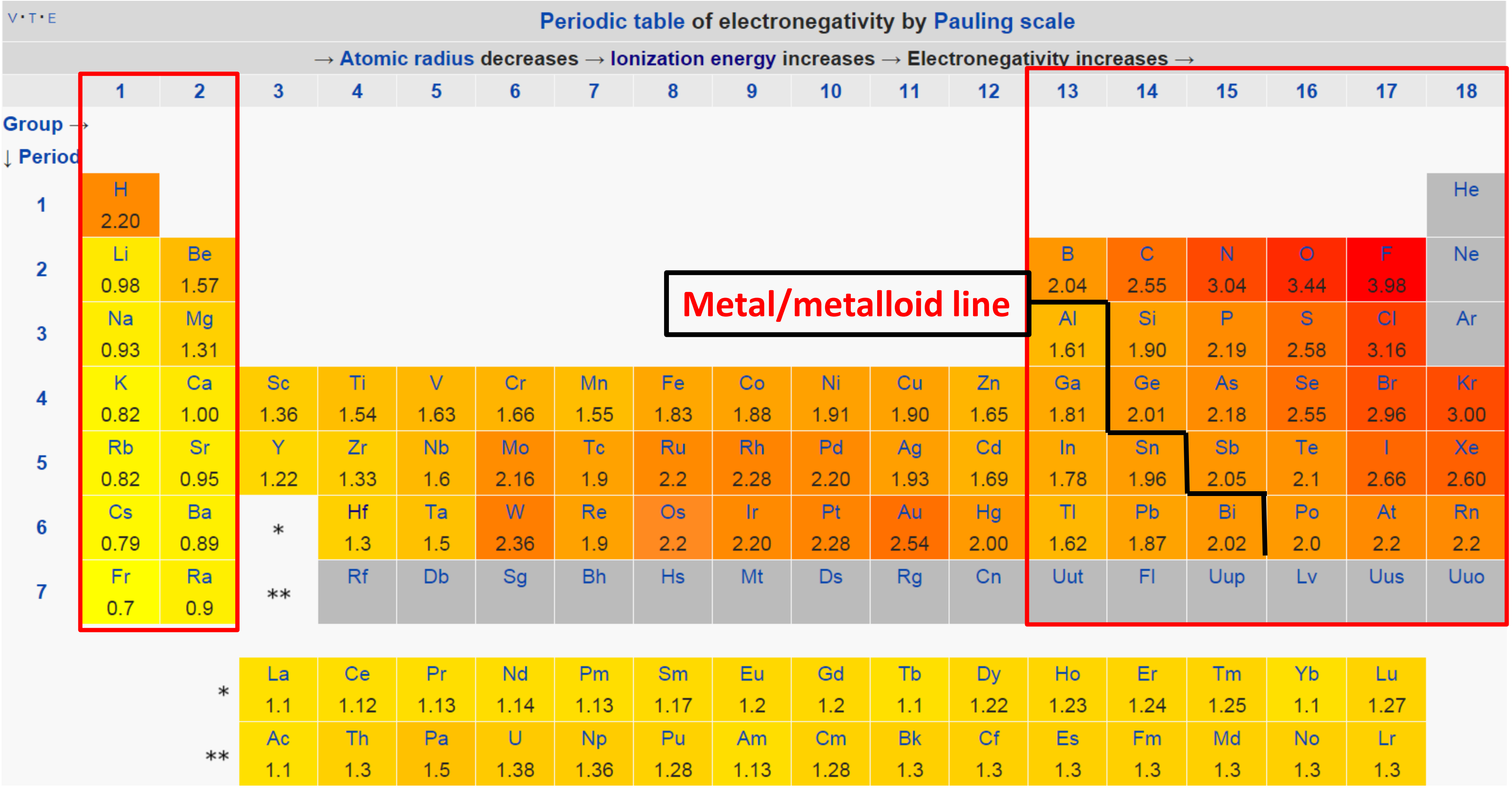
Zintl Ions

Principles and Recent Developments

Springer

Main group elements



Periodic table of electronegativity by Pauling scale

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

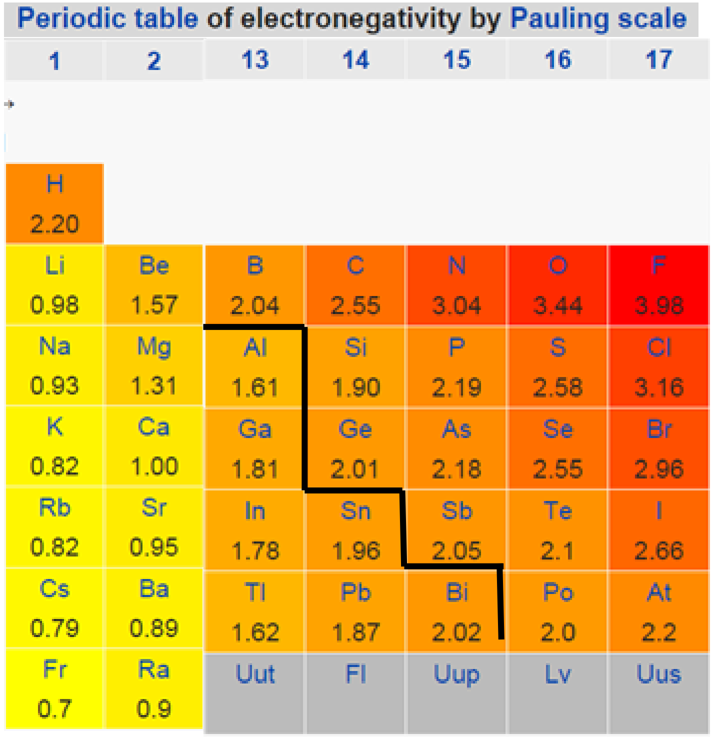
Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	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	

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

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

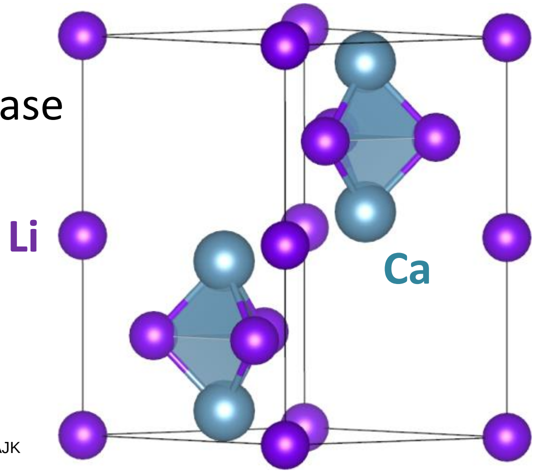
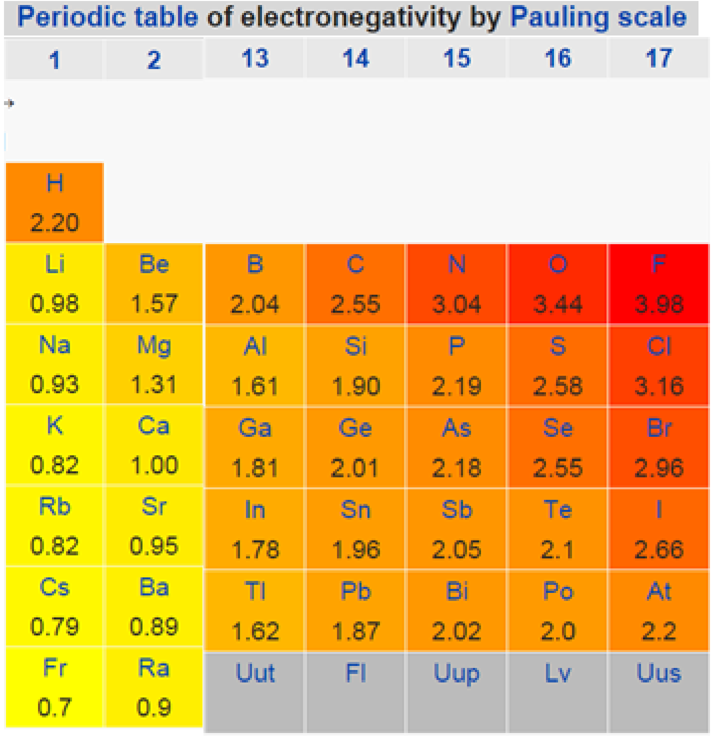


Figure: AJK

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



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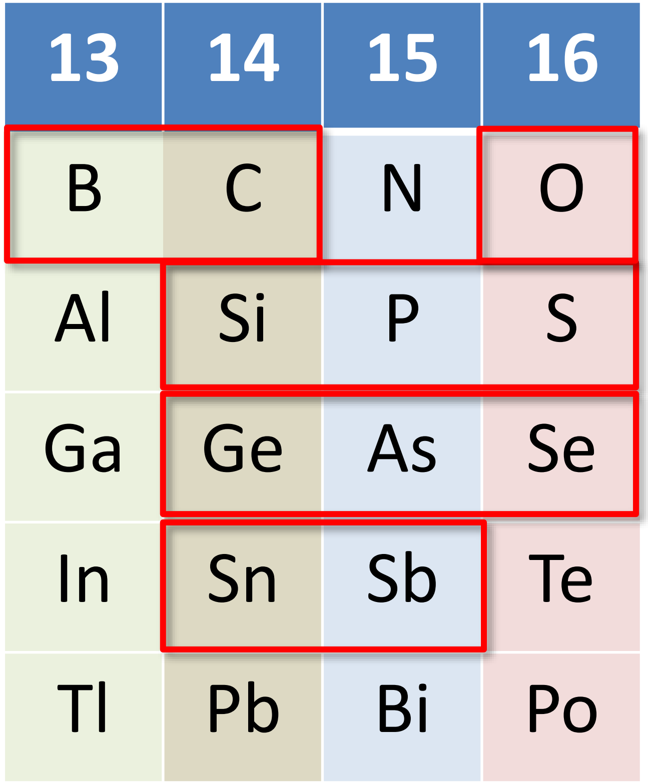
Fr 0.7	Ra 0.9	Uut	Fl	Uup	Lv	Uus

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 (= number and connectivity of atoms), but different composition (CO vs. N_2)

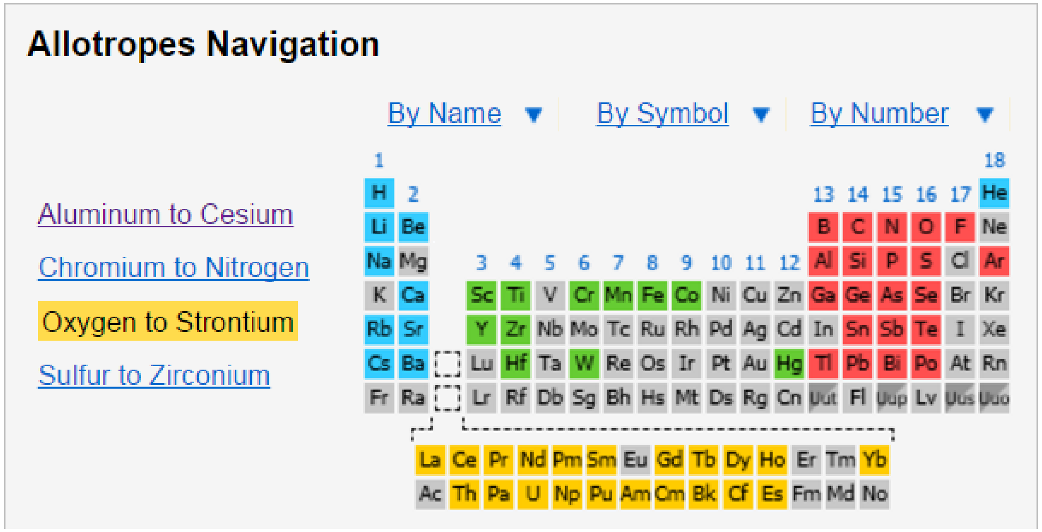


13	14	15	16
B	C	N	O
Al	Si	P	S
Ga	Ge	As	Se
In	Sn	Sb	Te
Tl	Pb	Bi	Po

Main groups 13-16, elements showing allotropy highlighted

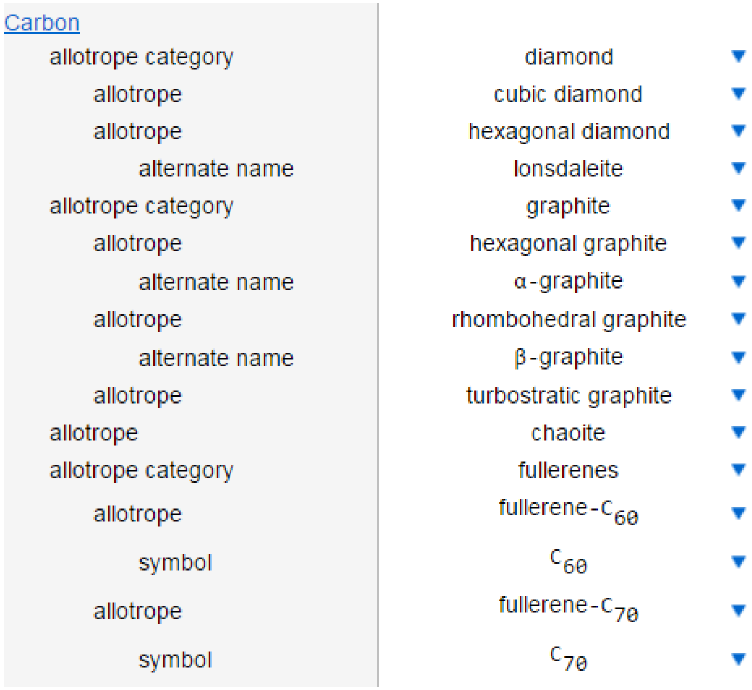
Allotropy

- 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 focus on few examples of group 14, 15, and 16 allotropes



Allotropes Navigation

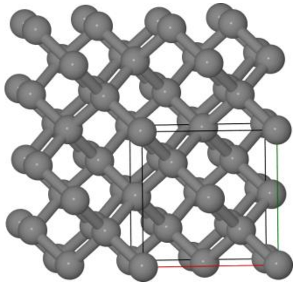
1																		18
H	2												13	14	15	16	17	He
Li	Be												B	C	N	O	F	Ne
Na	Mg		3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	⬚	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	⬚	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		



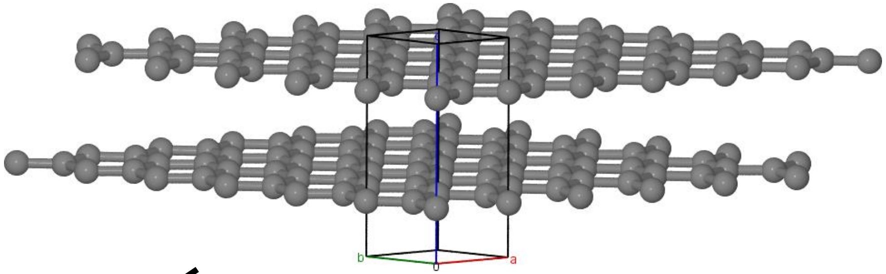
[Carbon]()

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}	▼

The allotropy of carbon



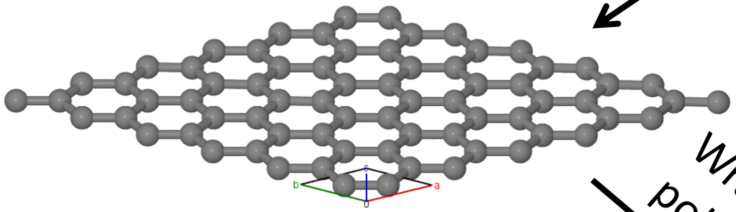
3D allotropes



Diamond (sp^3 bonding)

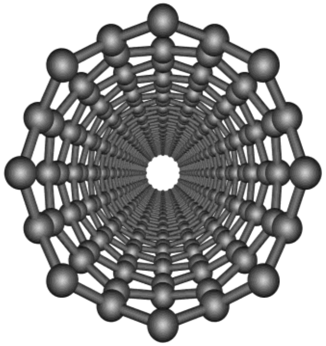
Graphite (sp^2 bonding)

Cut a slab

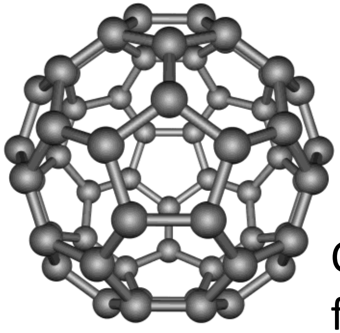


Graphene (2D)

Roll up to a tube



Wrap up to a polyhedron



Carbon nanotube (1D)

Carbon fullerene (0D)

Figures: 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)

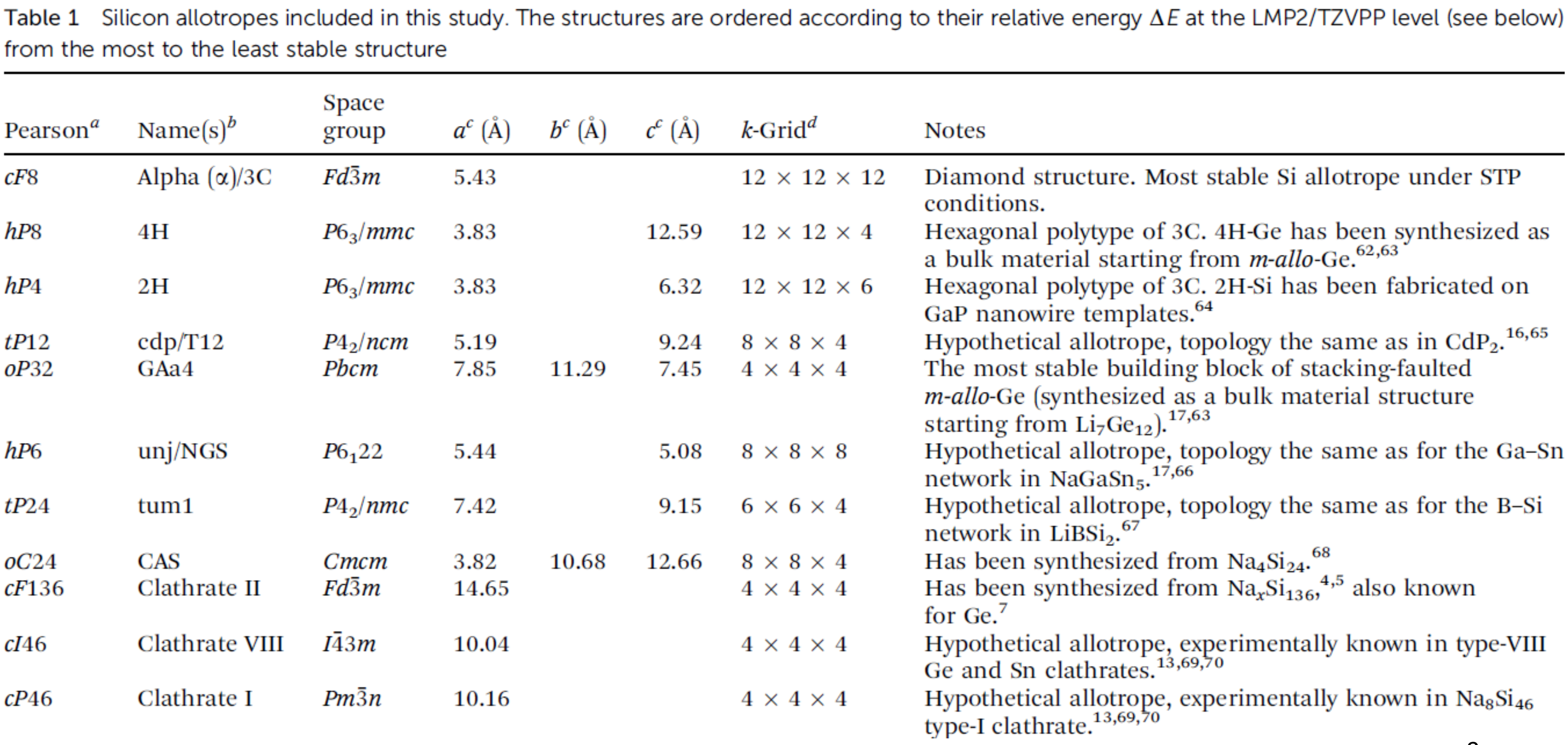
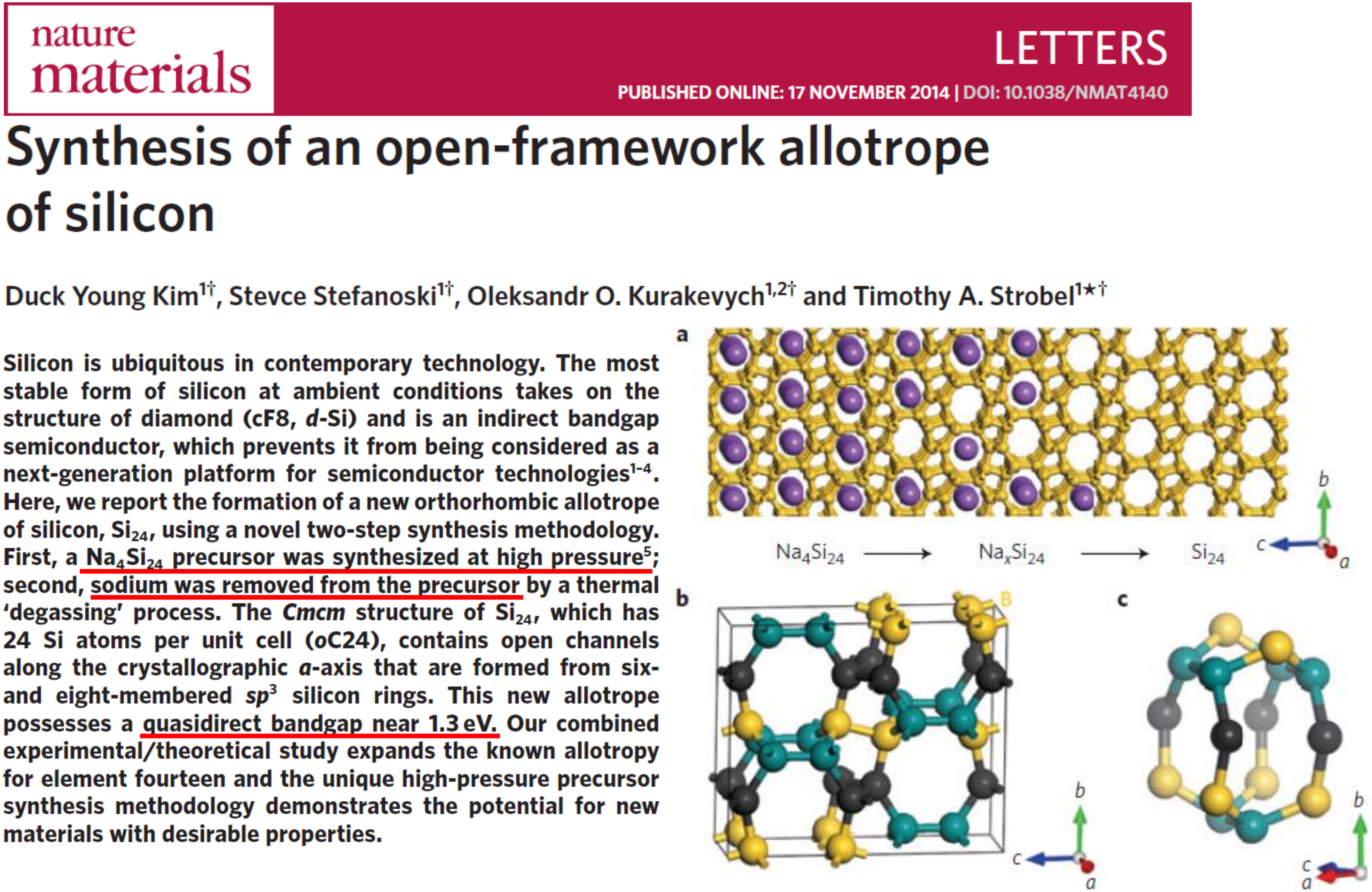


Table 1 Silicon allotropes included in this study. The structures are ordered according to their relative energy ΔE at the LMP2/TZVPP level (see below) from the most stable to the least stable structure

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

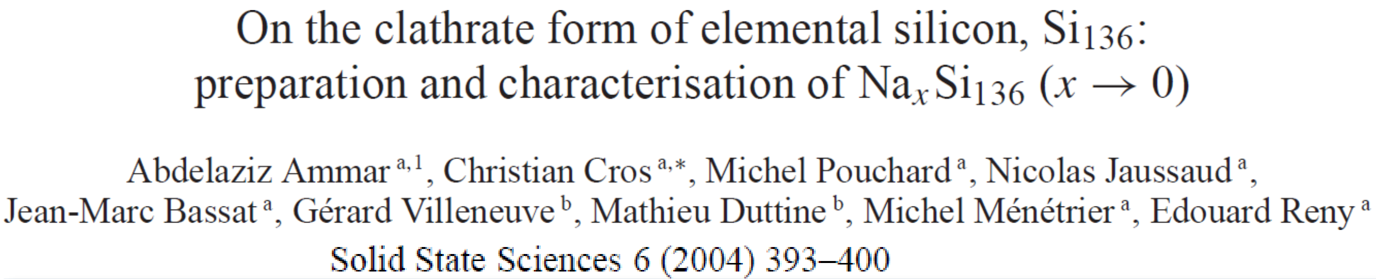
PUBLISHED ONLINE: 17 NOVEMBER 2014 | DOI: 10.1038/NMAT4140

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 (*o*C24), 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_xSi_{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**

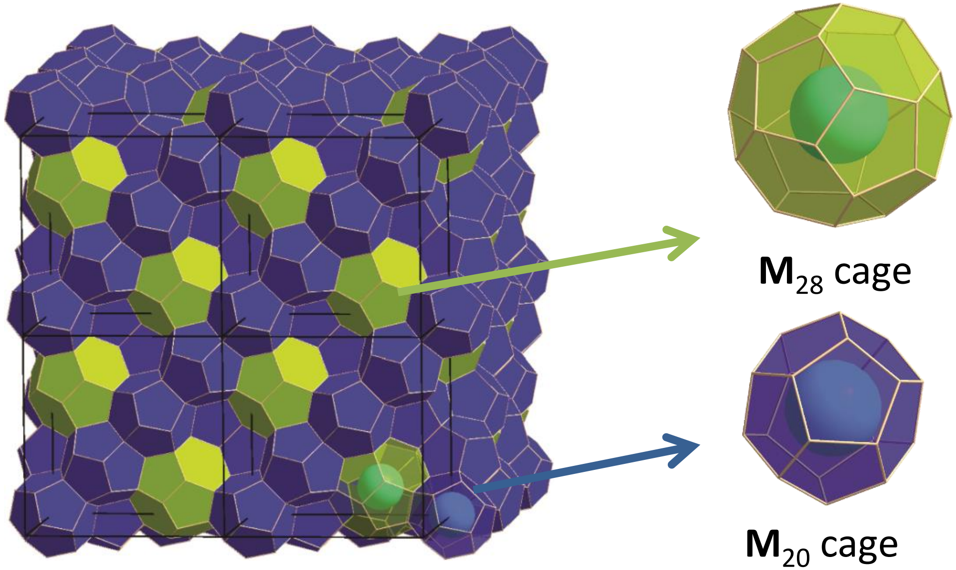
A guest-free germanium clathrate

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

Ionic liquid route, discussed in a later slide

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

Known for:
Si_{136}
Ge_{136}



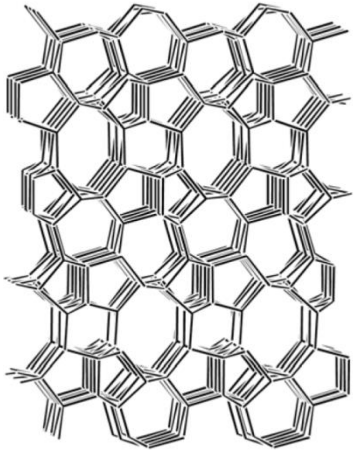
$\mathbf{M}_{28}$ cage

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

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

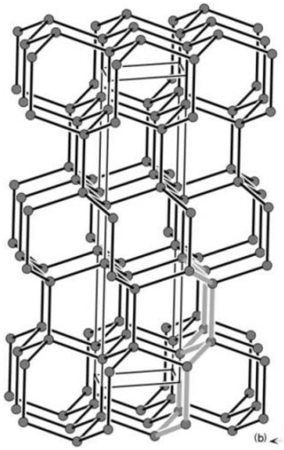
Ge and Sn allotropes

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



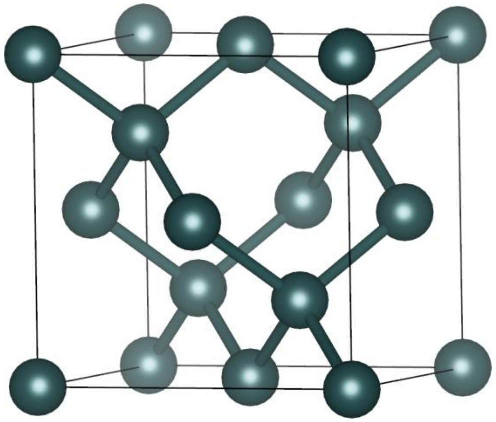
m-allo-Ge

140°C →



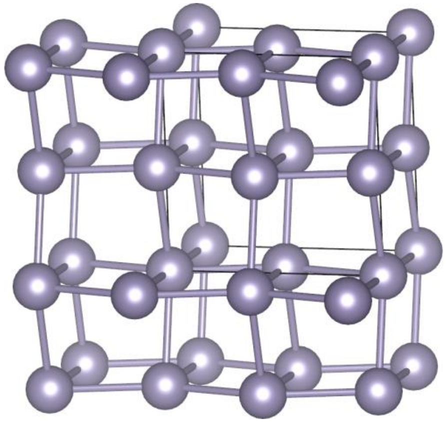
4H-Ge ($P6_3/mmc$)

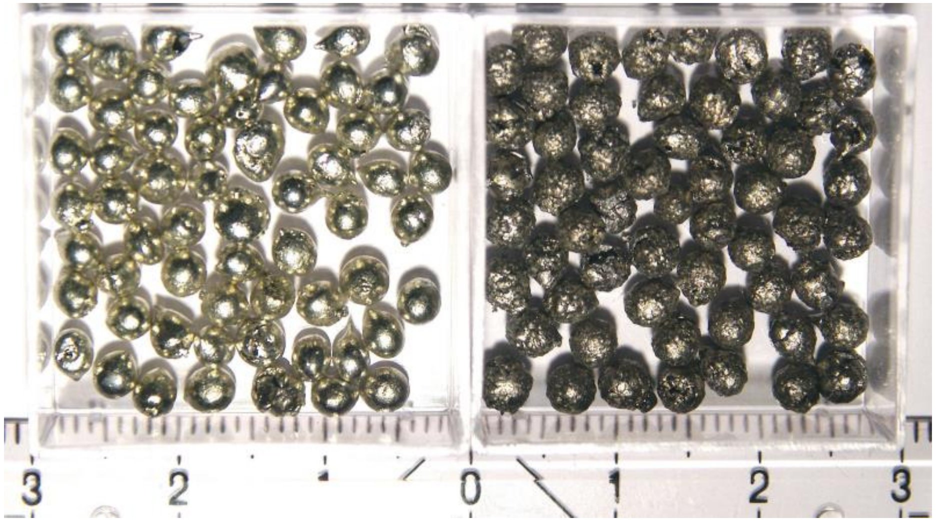
400°C →



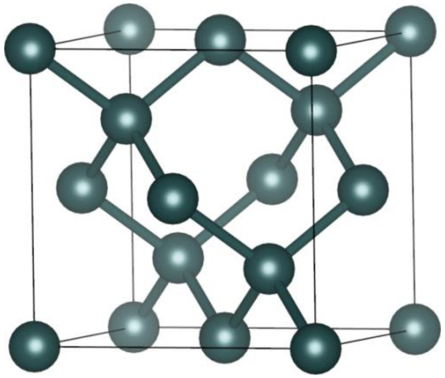
α-Ge (Fd-3m)

β-Sn ($I4_1/amd$)
white tin



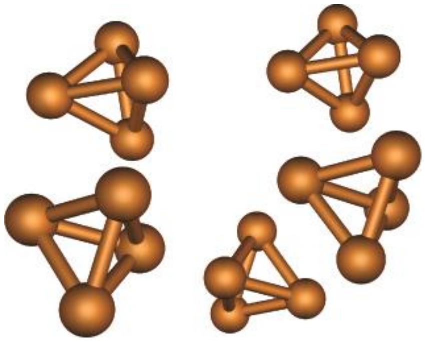


α-Sn (Fd-3m)
grey tin

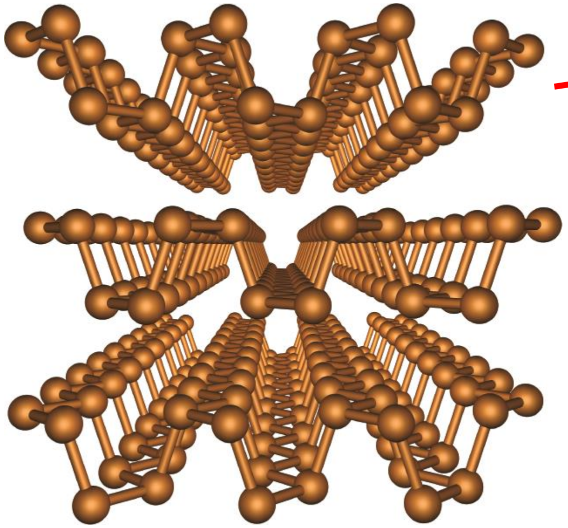


https://crystallography365.wordpress.com/2014/11/23/a-failed-campaign-alpha-and-beta-tin/
https://en.wikipedia.org/wiki/Tin_pest#Napoleon.27s_buttons

Group 15 allotropic modifications

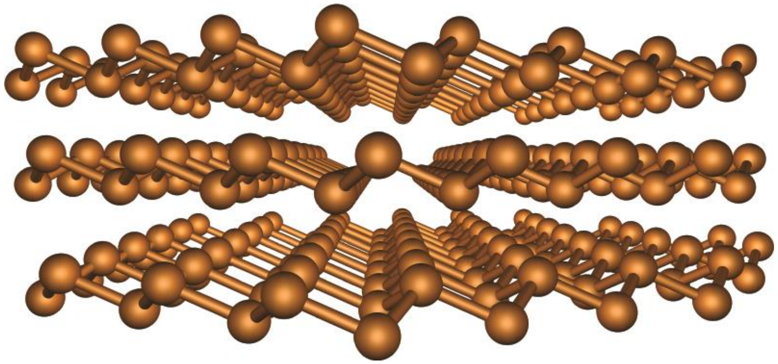


Tetrahedral molecules (P_4, As_4, Sb_4)
White phosphorus

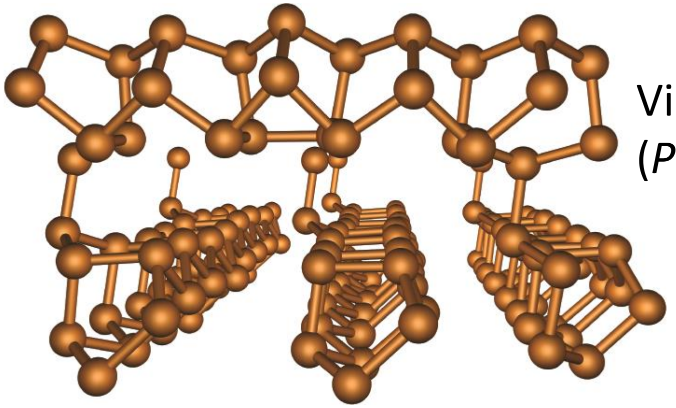


Individual sheets can be cleaved
-> phosphorene

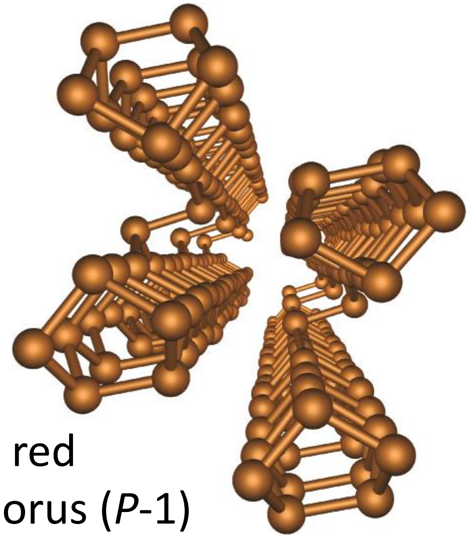
Orthorhombic layered structure, *Cmca* (P, As)
Black phosphorus



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



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



Fibrous red phosphorus (*P*-1)

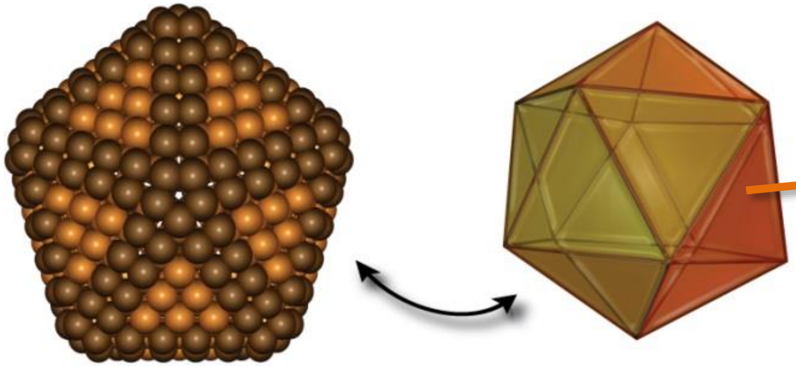
Figures: AJK

Phosphorus: The Allotropes Stability, Synthesis, and Selected Applications
T. Nilges, P. Schmidt, R. Weihrich, DOI: 10.1002/9781119951438.eibc2643

Group 15 nanostructures

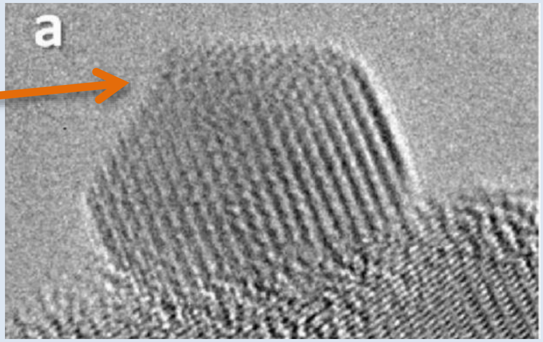
Analogous to the carbon fullerenes and nanotubes, but possess puckered atomic structure

Polyhedra (e.g. P_{180})



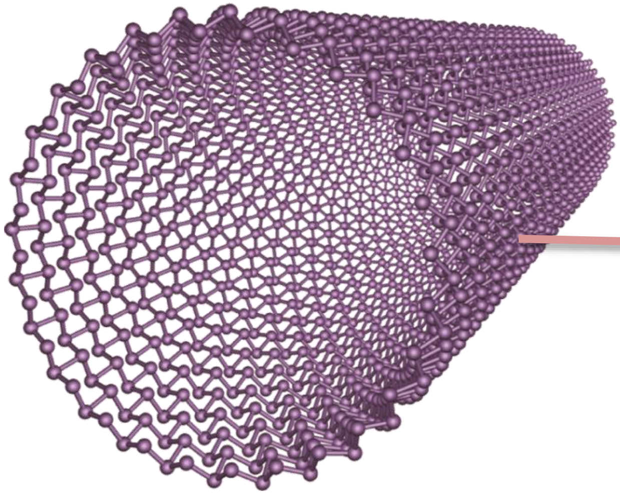
Chem. Eur. J. **2007**, *13*, 5232 (DOI)
Theor. Chem. Acc. **2011**, *129*, 412 (DOI)

Bismuth nanoicosahedra



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

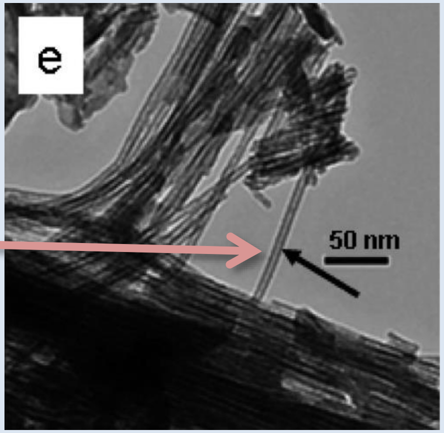
Nanotubes



Figures: AJK

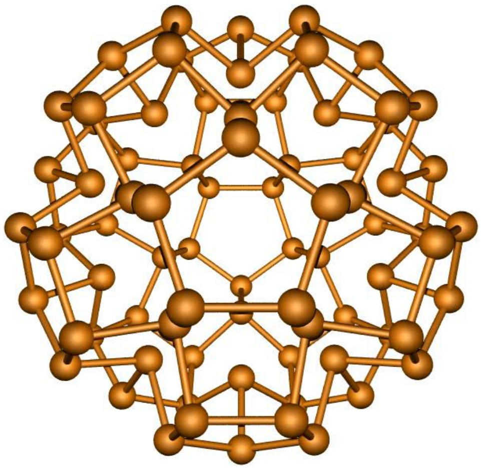
J. Phys. Chem. C **2009**, 113, 12220 (DOI)

Bismuth nanotubes

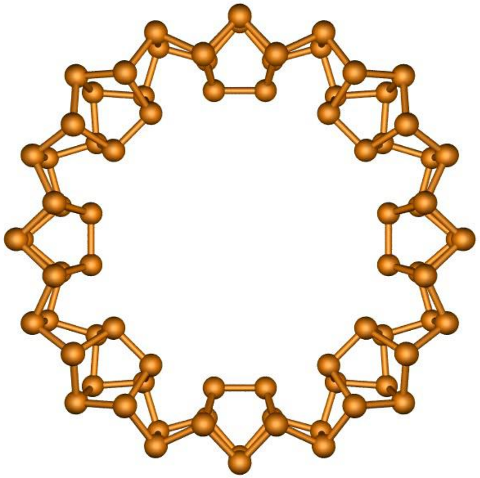


Pfefferle *et al*, *J. Phys. Chem. C*, **2010**, *114*, 3431.

Phosphorus nanostructures

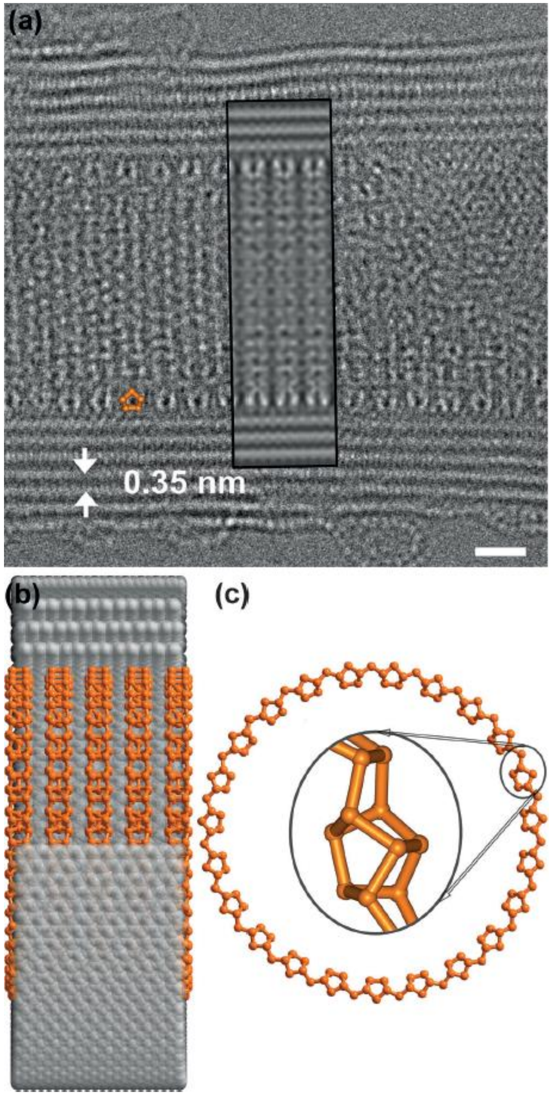


P_{80} fullerene (I_h)

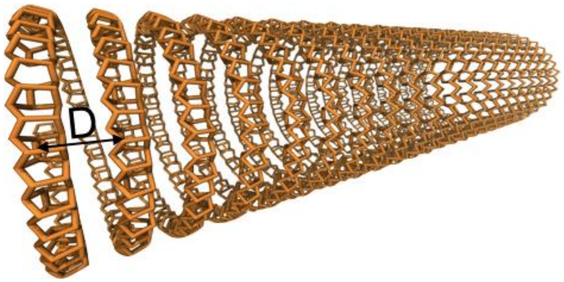


P_{80} ring (C_{4v})

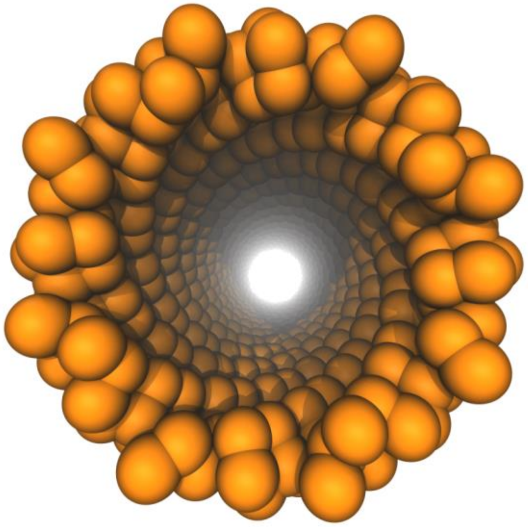
Icosahedral and Ring-shaped Allotropes of Phosphorus
Karttunen, A. J.; Linnolahti, M.; Pakkanen, T. A.
Chem. Eur. J. **2007**, *13*, 5232–5237 (DOI).



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



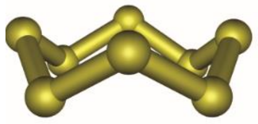
Red phosphorus helices



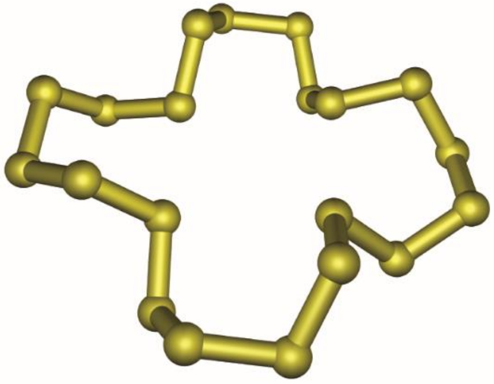
One-dimensional Phosphorus Nanostructures: from
Nanorings to Nanohelices
Sansone, G.; Maschio, L.; Karttunen, A. J. *Chem. Eur. J.*
2017, *23*, 15884–15888. (DOI).

Group 16 allotropes

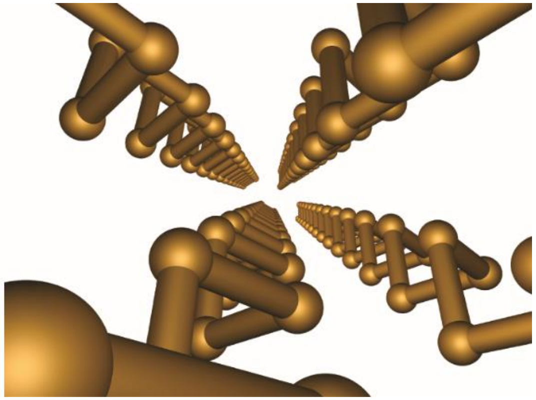
- Whereas the allotropes of group 15 elements are three-coordinate, the additional valence electron of group 16 elements makes their allotropes two-coordinate
- This imposes limits on the capability to form infinite structural networks, but the elemental chemistry of S and Se is still very rich
- The only known crystalline form of Te at room pressure is similar to gray Se



α-cyclo-S_8 (*Fddd*)



Cyclo-S_{20} (*Pbcn*)

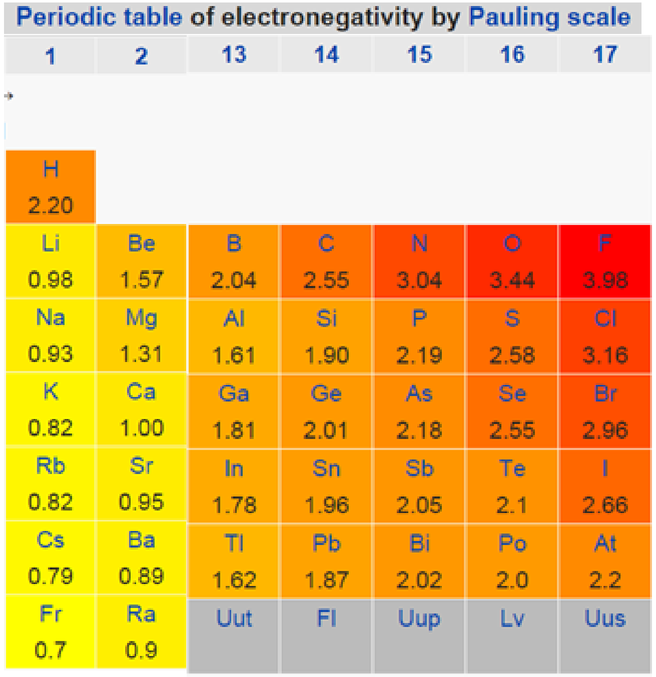


Gray selenium consisting of helical chains ($P3_121$)

Figures: AJK

Zintl phases

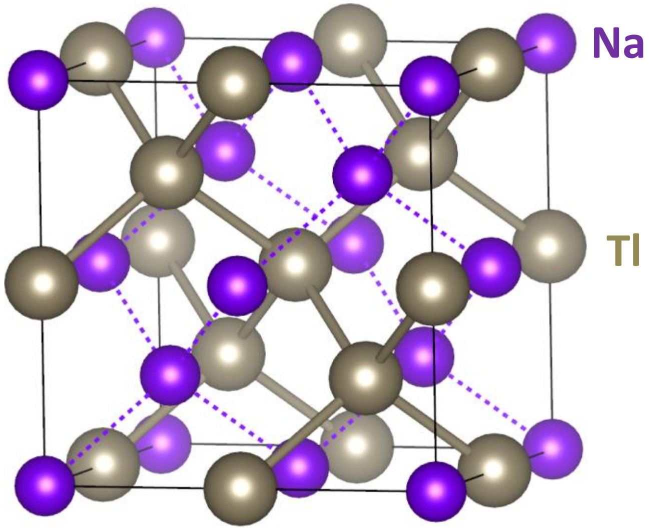
- Zintl phases are ***valence-balanced*** semiconductors
  - Charge transfer from Group 1 or 2 elements to Group 13-16 elements
- For example, NaTl (sodium thallide)
  - Each Na atom donates $1e^-$
  - Each Tl atom accepts $1e^-$
- The electron configuration of the anionic Tl network is now **analogous 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

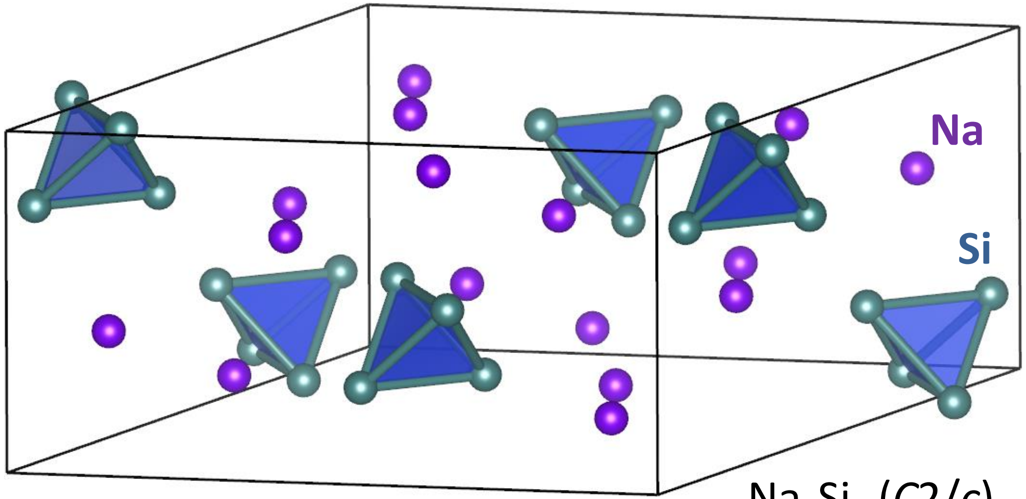
Examples of Zintl phases (1)

NaSi (Na_4Si_4)

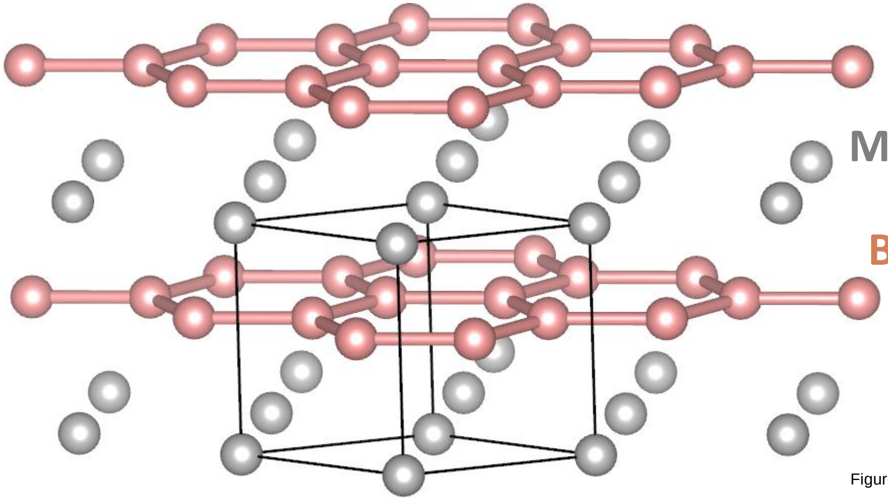
- Each Na atom donates $1e^-$
- Each Si atom accepts $1e^-$
- Si_4^{4-} tetrahedra are isoelectronic with P_4 tetrahedra (white phosphorus)

MgB_2

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



Na_4Si_4 ($C2/c$)



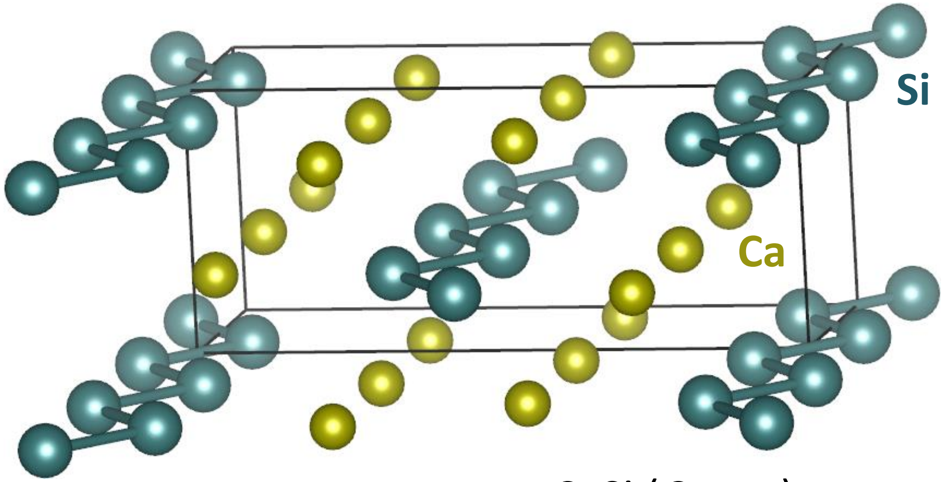
MgB_2 ($P6/mmm$)

Figures: AJK

Examples of Zintl phases (2)

CaSi

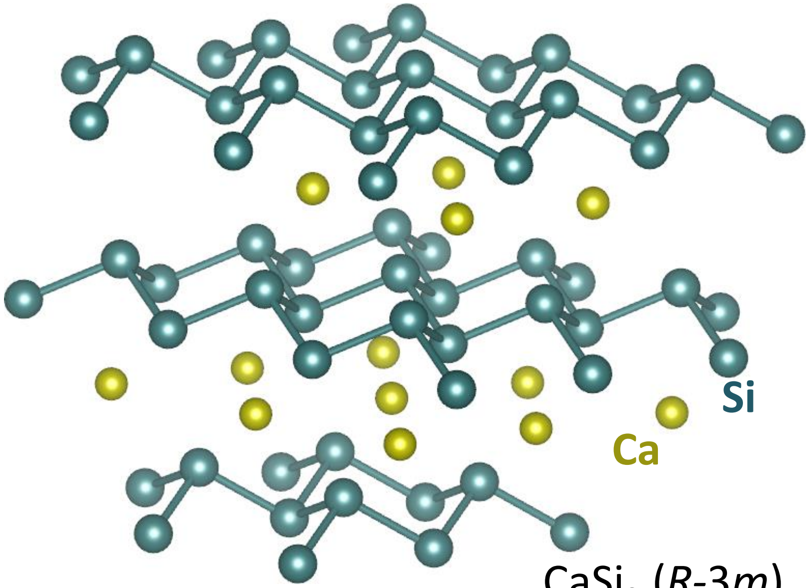
- Each Ca atom donates 2e^{-}
- Each Si atom accepts 2e^{-}
- The resulting one-dimensional Si-chains are closely related to Se-chains (but planar, not helical)



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

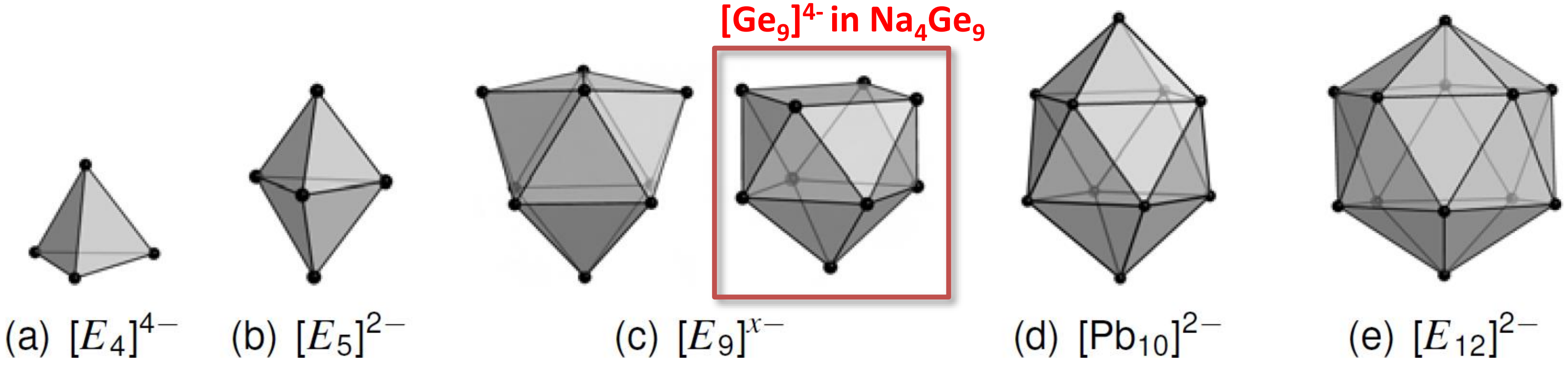


CaSi$_2$ (*R*-3*m*)

Figures: AJK

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

Many solid-state Zintl phases contain discrete anions



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

Figure: Sandra Scharfe / Dissertation 2010 (TUM)

For example, $[\mathrm{Ge}_9]^{4-}$ in $\mathrm{Na}_4\mathrm{Ge}_9$

$[\mathrm{Si}_4]^{4-}$ in $\mathrm{Na}_4\mathrm{Si}_4$

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

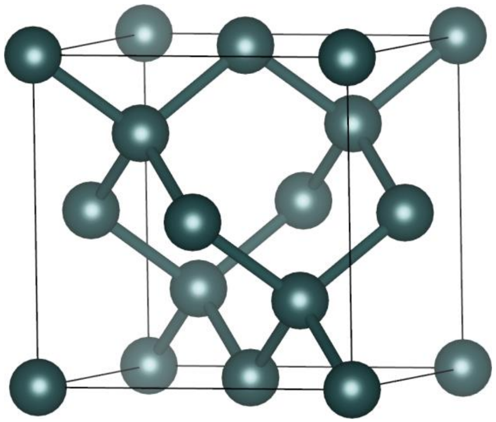
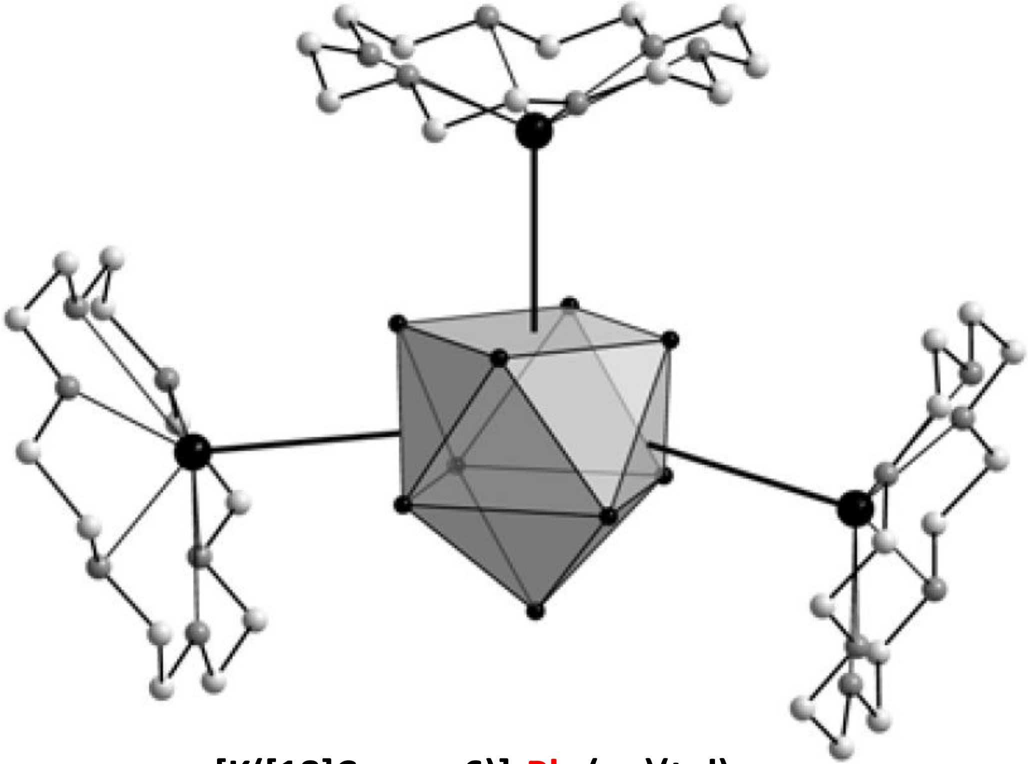


Figure: AJK

Zintl Ions, Cage Compounds, and Intermetalloid Clusters of Group 14 and Group 15 Elements, S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chem. Int. Ed.* **2011**, *50*, 3630–3670 (DOI).

Zintl ions can be crystallized from solution



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

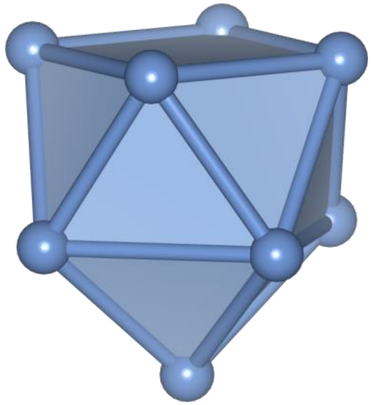
S. Scharfe, Dissertation, Technical University of Munich, **2010**

Zintl phases as precursors for preparing novel materials

NATURE|Vol 443|21 September 2006 **LETTERS**

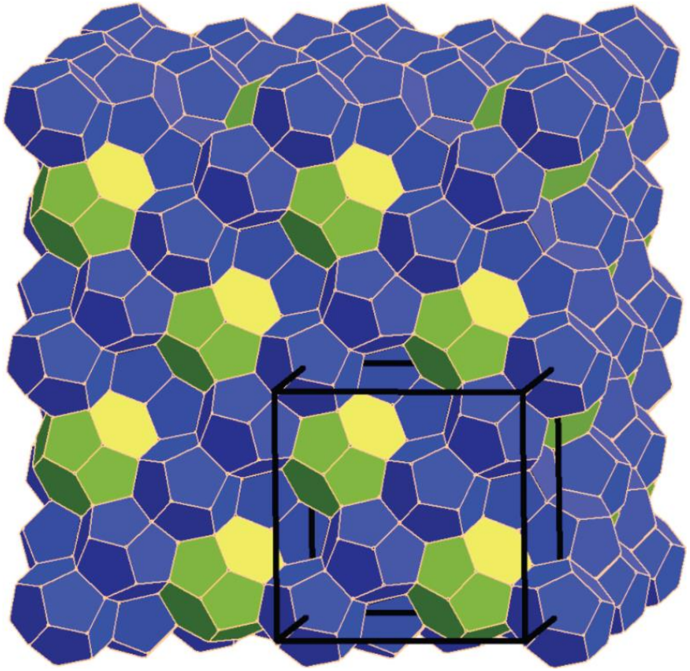
A guest-free germanium clathrate

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

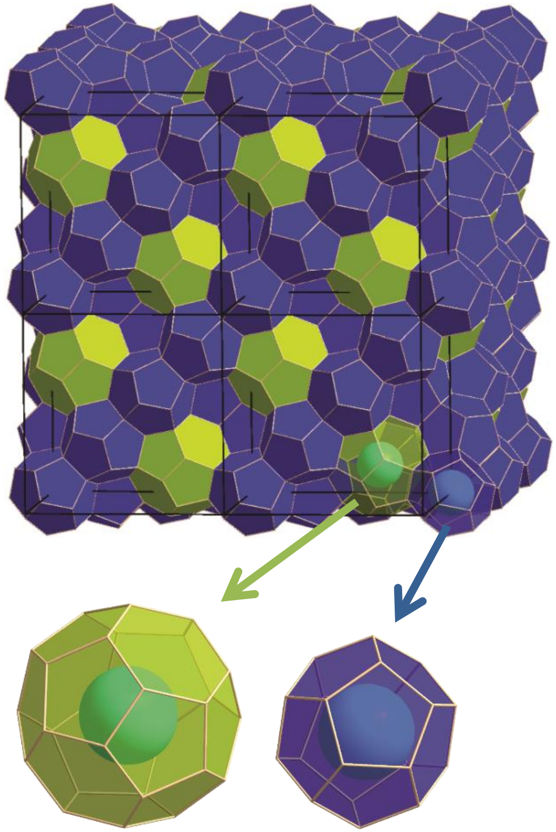


Ge_{136} Clathrate-II (*cF*136)

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*)



M$_{28}$ cage **M**$_{20}$ cage

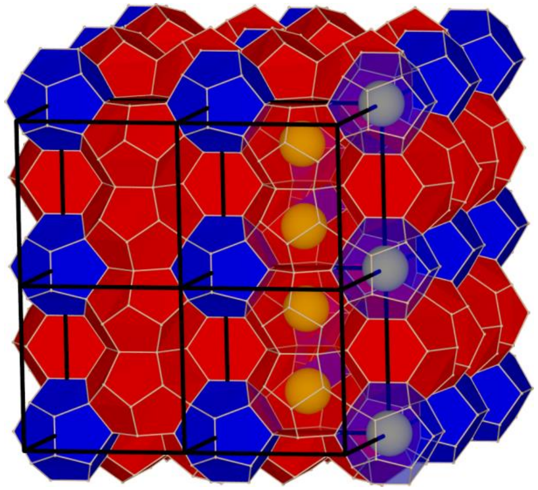
(**M** = Si, Ge, Sn)

[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)



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

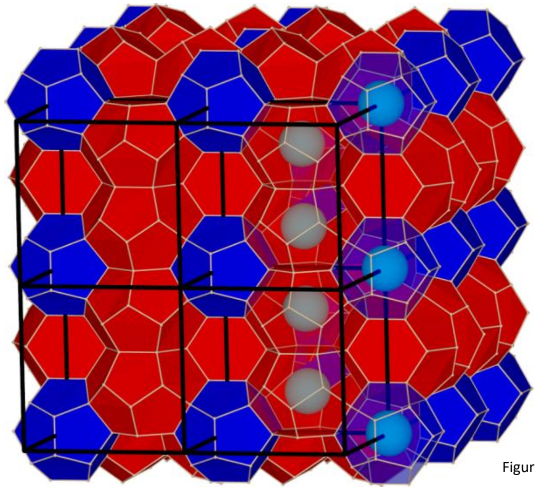
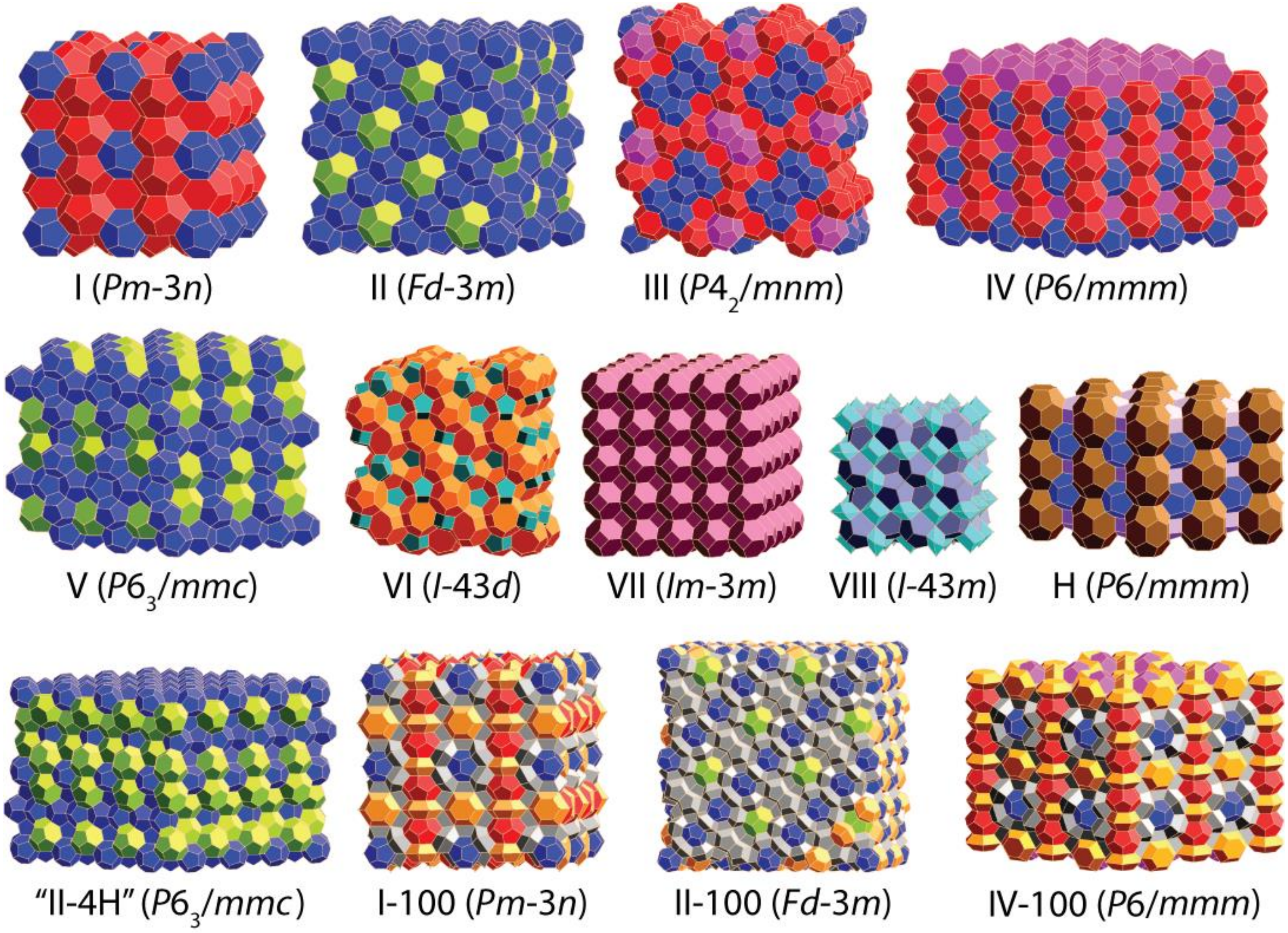


Figure: AJK

- $I_8[As_8Ge_{38}]$ (**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)



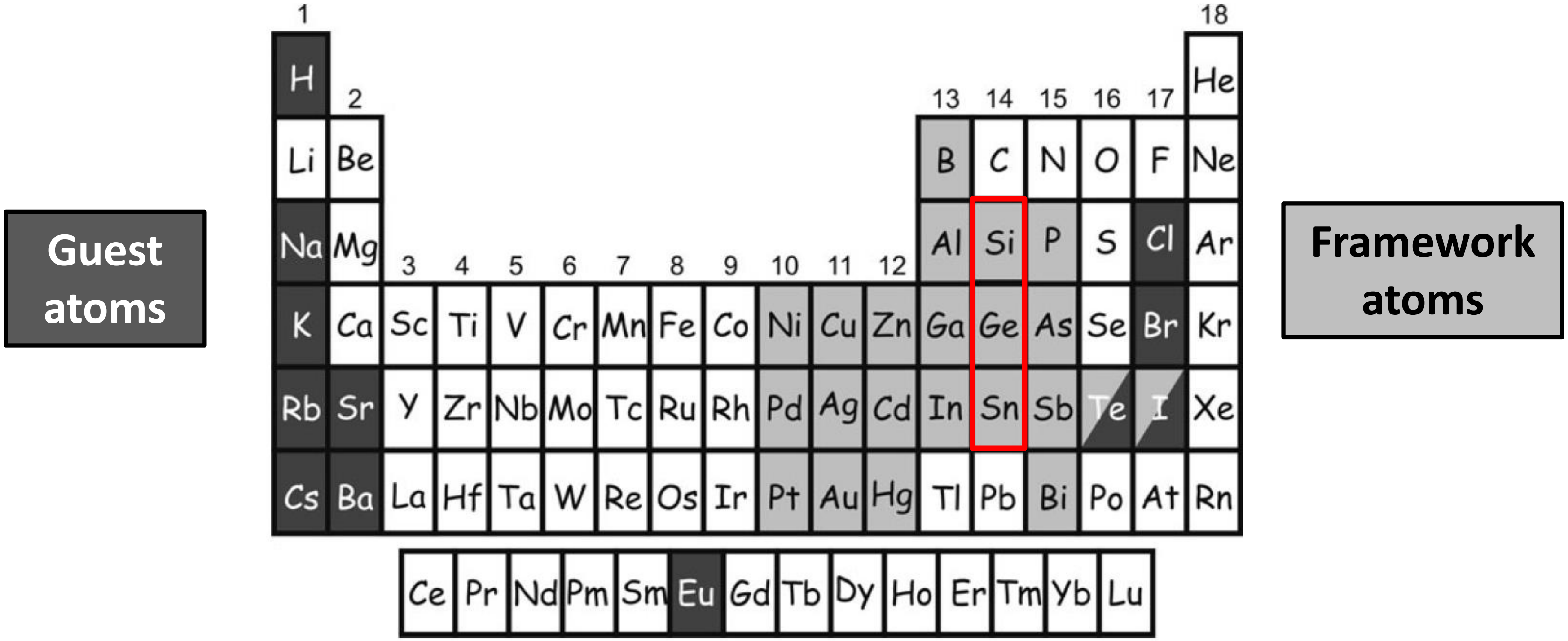
I (*Pm*-3*n*) II (*Fd*-3*m*) III ($P4_2/mnm$) IV (*P6*/*mmm*)

V ($P6_3/mmc$) VI (*I*-43*d*) VII (*Im*-3*m*) VIII (*I*-43*m*) H (*P6*/*mmm*)

"II-4H" ($P6_3/mmc$) I-100 (*Pm*-3*n*) II-100 (*Fd*-3*m*) IV-100 (*P6*/*mmm*)

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

Currently known group 14 clathrates



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

$Na_8[Si_{46}]$

$Na_{8-x}Ba_x[Si_{46}]$

$Na_xBa_6[Si_{46}]$

$K_{7.62}\square_{0.38}[Si_{46}]$

$Rb_{6.15}\square_{1.85}[Si_{46}]$

$K_8[Ga_8Si_{38}]$

$Rb_8[Al_8Si_{38}]$

$Rb_8[Ga_8Si_{38}]$

Ge-based

$K_8[Al_8Ge_{38}]$

$Rb_8[Al_8Ge_{38}]$

$K_8[Ga_8Ge_{38}]$

$Rb_8[Ga_8Ge_{38}]$

$Cs_8[Ga_8Ge_{38}]$

$K_8[In_8Ge_{38}]$

$Rb_8[In_8Ge_{38}]$

$Cs_8[In_8Ge_{38}]$

Ge-based

$I_8[Ge_{38}P_8]$

$Br_8[Ge_{38}P_8]$

$Cl_8[Ge_{38}P_8]$

$I_8[Ge_{38}As_8]$

$Br_8[Ge_{38}As_8]$

$Cl_8[Ge_{38}As_8]$

$I_8[Ge_{38}Sb_8]$

$Br_8[Ge_{38}Sb_8]$

$I_8[Ge_{14}Ga_{12}Sb_{20}]$

Sn-based

$K_{1.6}Cs_{6.4}[Sn_{44}\square_2]$

$Rb_8[Sn_{44.6}\square_{1.4}]$

$Cs_8[Sn_{44}\square_2]$

$K_8[Al_8Sn_{38}]$

$Rb_8[Al_8Sn_{38}]$

$K_8[Ga_8Sn_{38}]$

$Rb_8[Ga_8Sn_{38}]$

$Cs_8[Ga_8Sn_{38}]$

$Cs_8[Zn_4Sn_{42}]$

$Cs_8[Cd_4Sn_{42}]$

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