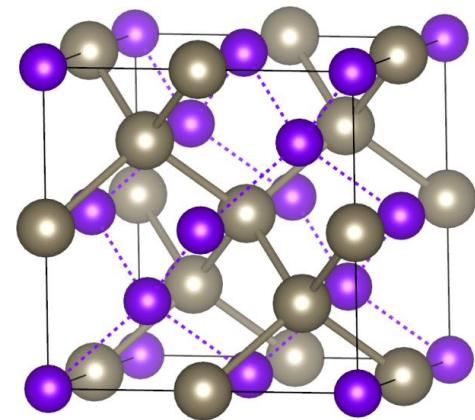
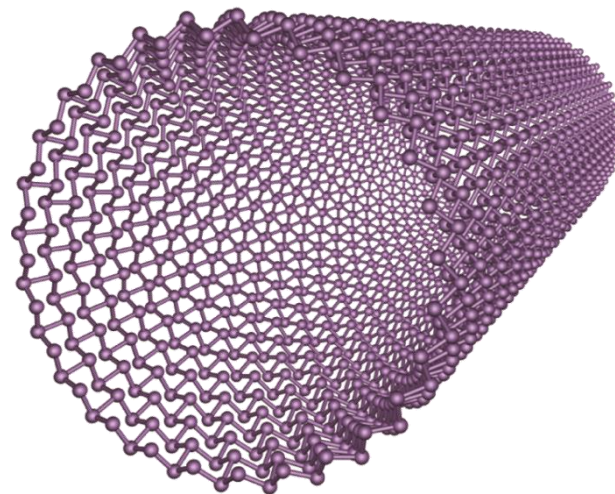


# Lecture 10:

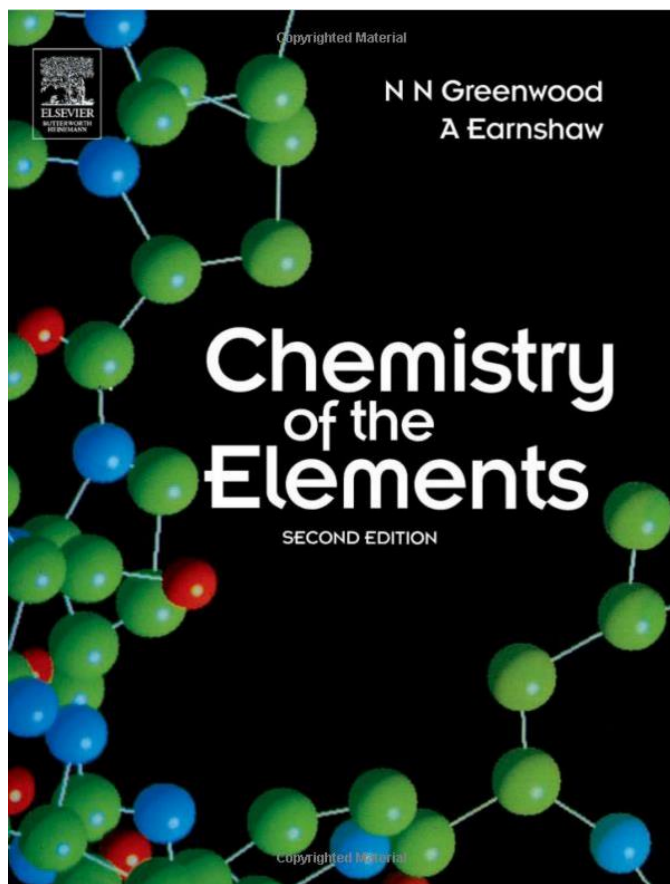
## Main group compounds

- 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



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

Thomas F. Fässler *Editor*

## 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 →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
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 that relevant, but some interesting examples such as Laves phase  $\text{CaLi}_2$
- Groups 1 + 17 and groups 2 + 17 ( $\text{NaCl}$ ,  $\text{MgCl}_2$ , ...)
- 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 (e.g.  $\text{SiCl}_4$ ,  $\text{PCl}_5$ ,  $\text{SF}_6$ )
  - Mostly **non-molecular** for Al, Ga, In, Tl, Pb
  - Almost follows metal/metalloid line
- Oxides
  - Simple salts for groups 1 and 2 (e.g.  $\text{MgO}$ )
  - Stable oxides for groups 13-16, not for 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

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

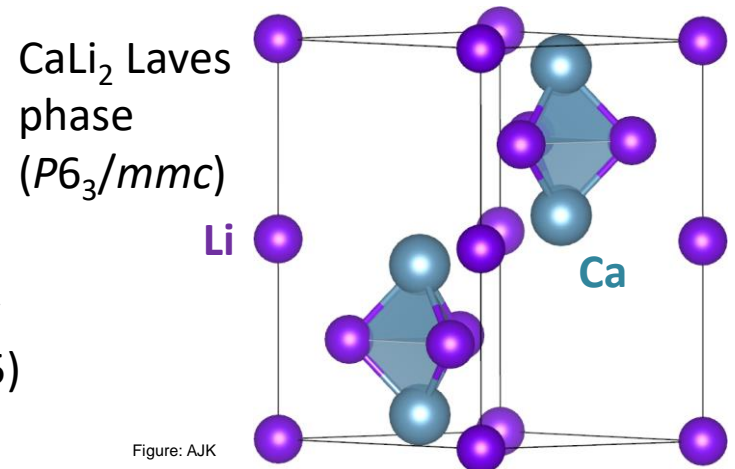


Figure: AJK

# Overview of main group compounds (2)

- Group 1/2 + 14: Carbides, silicides, germanides, ...
  - $\text{CaC}_2$ ,  $\text{Mg}_2\text{Si}$ ,  $\text{CaGe}_2$ , ...
- Group 1/2 + 15: Nitrides, phosphides, arsenides, ...
  - $\text{Li}_3\text{N}$ ,  $\text{Li}_3\text{P}$ ,  $\text{Li}_3\text{As}$ , ...
- Main group compound semiconductors
  - 13-15 (BN, GaN, GaAs, etc.)
  - 14-16 (PbTe, PbSnTe, SnS, etc.)
  - 15-16 ( $\text{Sb}_2\text{Se}_3$ ,  $\text{Bi}_2\text{Te}_3$ , etc.)
- Some elements are technologically extremely important as such or as simple alloys/compounds
  - Si, Ge,  $\text{Si}_x\text{Ge}_{1-x}$ , 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
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

# 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<sub>2</sub>)

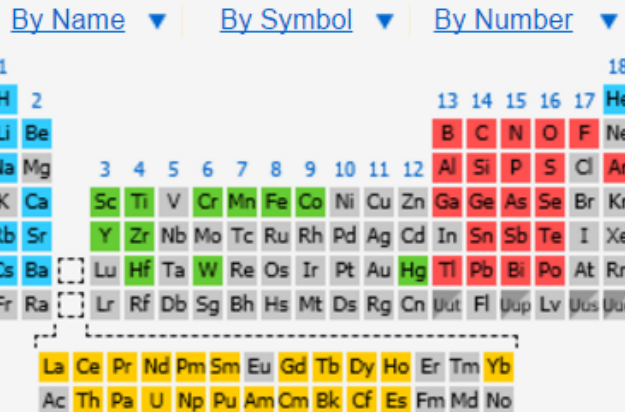
13	14	15	16
B	C	N	O
Al	Si	P	S
Ga	Ge	As	Se
In	Sn	Sb	Te
Tl	Pb	Bi	Po

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](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

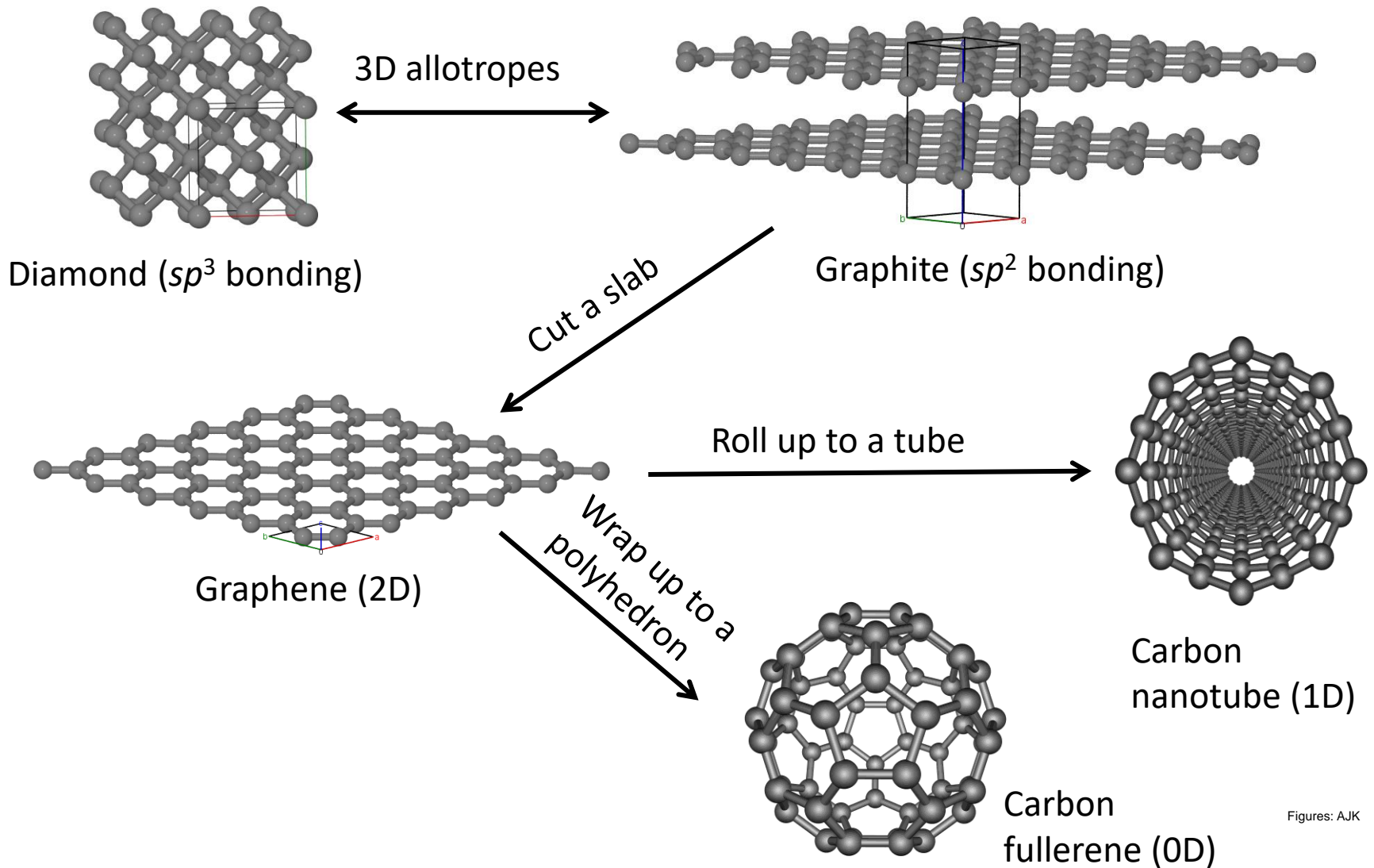
## Allotropes Navigation



## 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 <sub>60</sub>	▼
symbol	C <sub>60</sub>	▼
allotrope	fullerene-C <sub>70</sub>	▼
symbol	C <sub>70</sub>	▼

# The allotropy of carbon





# Some allotropes of Si and Ge

Name(s)	Space group	Notes
<b>Alpha (<math>\alpha</math>) / 3C</b>	<i>Fd-3m</i>	Diamond structure. Most stable Si and Ge allotrope at ambient $T$ and $p$ .
<b>2H</b>	<i>P6<sub>3</sub>/mmc</i>	Hexagonal polytype of 3C. <b>2H-Si</b> has been fabricated on GaP nanowire templates.
<b>4H</b>	<i>P6<sub>3</sub>/mmc</i>	Hexagonal polytype of 3C. <b>4H-Ge</b> has been synthesized as bulk material starting from <i>m-allo-Ge</i> .
<b>cdp / T12</b>	<i>P4<sub>2</sub>/ncm</i>	Hypothetical allotrope, topology same as in CdP <sub>2</sub> .
<b>GAa4</b>	<i>Pbcm</i>	The most stable building block of stacking-faulted <i>m-allo-Ge</i> (synthesized as bulk material structure starting from Li <sub>7</sub> Ge <sub>12</sub> ).
<b>unj / NGS</b>	<i>P6<sub>1</sub>22</i>	Hypothetical allotrope, topology same as for the Ga-Sn network in NaGaSn <sub>5</sub> .
<b>tum1</b>	<i>P4<sub>2</sub>/nmc</i>	Hypothetical allotrope, topology same as for the B-Si network in LiBSi <sub>2</sub> .
<b>CAS</b>	<i>Cmcm</i>	Has been synthesized from Na <sub>4</sub> Si <sub>24</sub> .
<b>Clathrate II</b>	<i>Fd-3m</i>	Has been synthesized from Na <sub>x</sub> Si <sub>136</sub> , also known for Ge.
<b>Clathrate VIII</b>	<i>I-43m</i>	Hypothetical allotrope, experimentally known in type-VIII Ge and Sn clathrates.
<b>Clathrate I</b>	<i>Pm-3n</i>	Hypothetical allotrope, experimentally known in Na <sub>8</sub> Si <sub>46</sub> type-I clathrate.

Source: 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](https://doi.org/10.1039/c6cp08873b))

# Open-framework allotrope of Si

nature  
materials

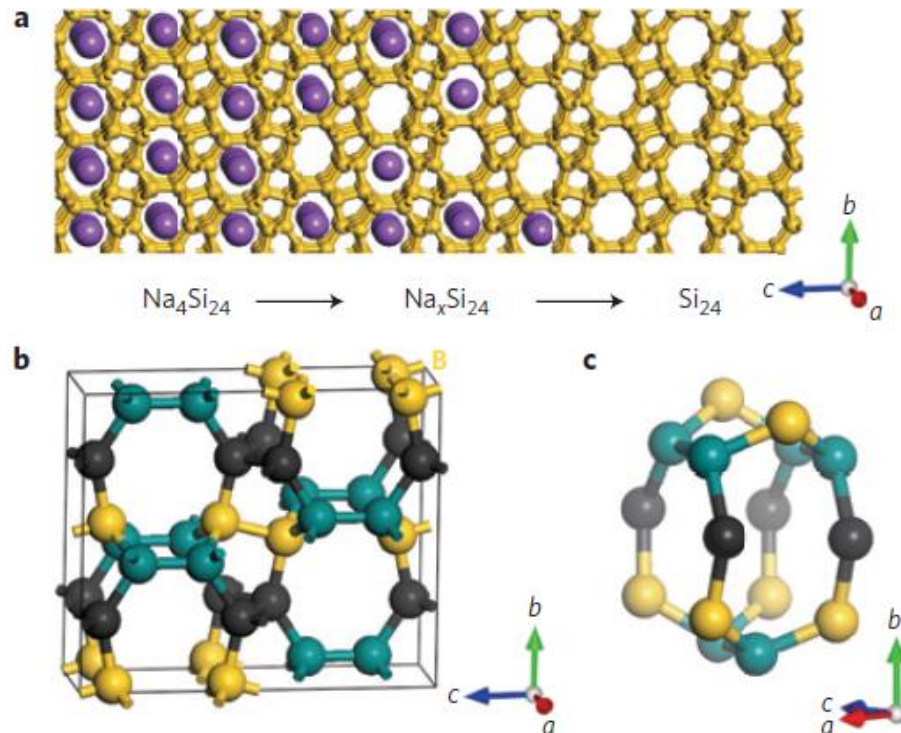
LETTERS

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

## Synthesis of an open-framework allotrope of silicon

Duck Young Kim<sup>1†</sup>, Stevce Stefanoski<sup>1†</sup>, Oleksandr O. Kurakevych<sup>1,2‡</sup> and Timothy A. Strobel<sup>1\*†</sup>

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<sup>1–4</sup>. Here, we report the formation of a new orthorhombic allotrope of silicon, Si<sub>24</sub>, using a novel two-step synthesis methodology. First, a Na<sub>4</sub>Si<sub>24</sub> precursor was synthesized at high pressure<sup>5</sup>; second, sodium was removed from the precursor by a thermal 'degassing' process. The *Cmcm* structure of Si<sub>24</sub>, 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*<sup>3</sup> 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<sub>136</sub> and Ge<sub>136</sub> allotropes

On the clathrate form of elemental silicon, Si<sub>136</sub>:  
preparation and characterisation of Na<sub>x</sub>Si<sub>136</sub> ( $x \rightarrow 0$ )

Abdelaziz Ammar<sup>a,1</sup>, Christian Cros<sup>a,\*</sup>, Michel Pouchard<sup>a</sup>, Nicolas Jaussaud<sup>a</sup>,  
Jean-Marc Bassat<sup>a</sup>, Gérard Villeneuve<sup>b</sup>, Mathieu Duttine<sup>b</sup>, Michel Ménétrier<sup>a</sup>, Edouard Reny<sup>a</sup>  
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

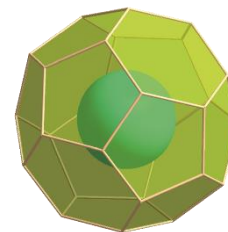
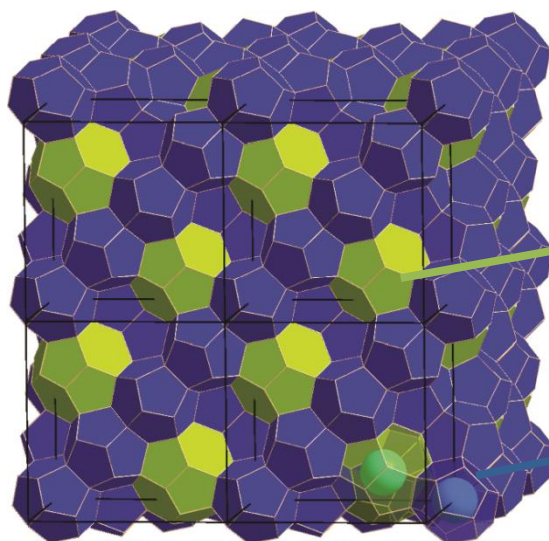
Arnold M. Guloy<sup>1,2</sup>, Reiner Ramlau<sup>1</sup>, Zhongjia Tang<sup>1,2</sup>, Walter Schnelle<sup>1</sup>, Michael Baitinger<sup>1</sup> & Yuri Grin<sup>1</sup>

Clathrate-II  
(*Fd-3m*)

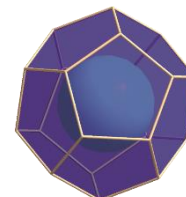
Known for:

Si<sub>136</sub>

Ge<sub>136</sub>



M<sub>28</sub> cage

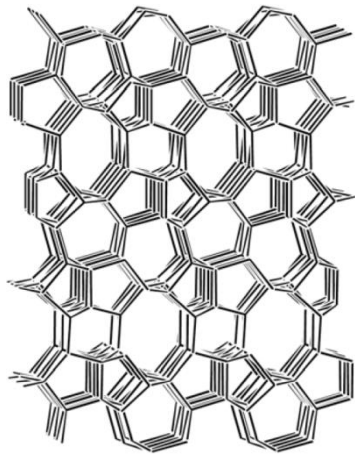


M<sub>20</sub> cage

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

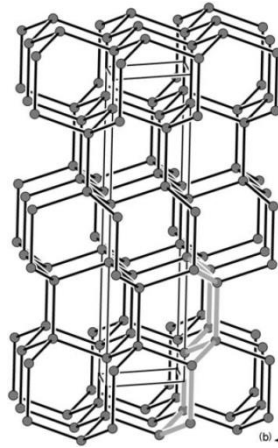
# Ge and Sn allotropes

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



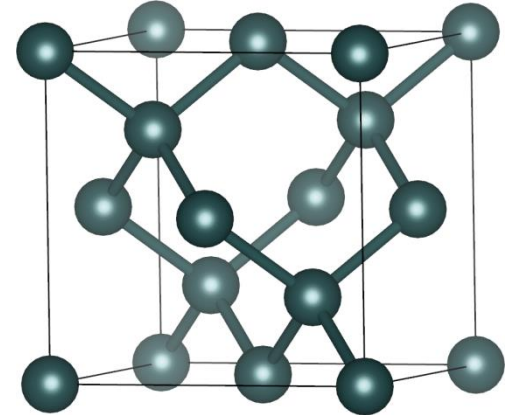
*m*-allo-Ge

140°C



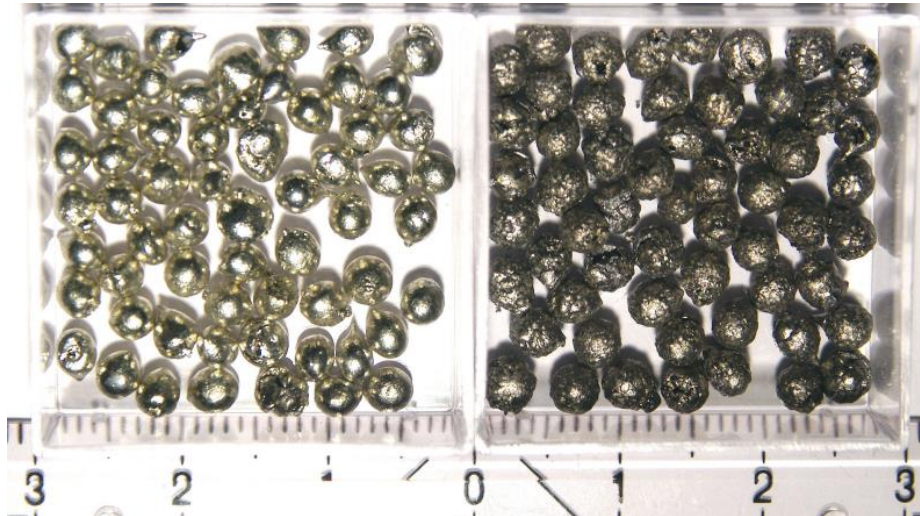
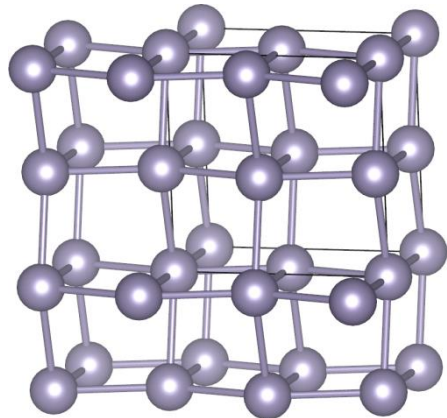
4H-Ge ( $P6_3/mmc$ )

400°C

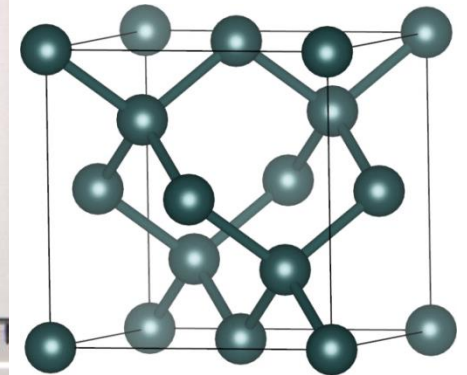


$\alpha$ -Ge ( $Fd-3m$ )

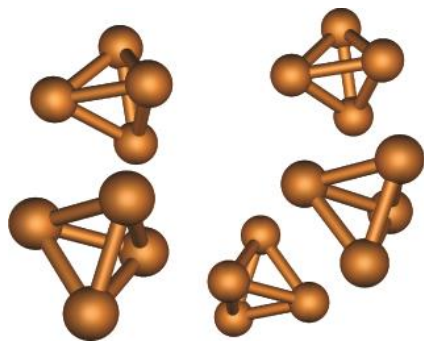
$\beta$ -Sn ( $I4_1/amd$ )  
white tin



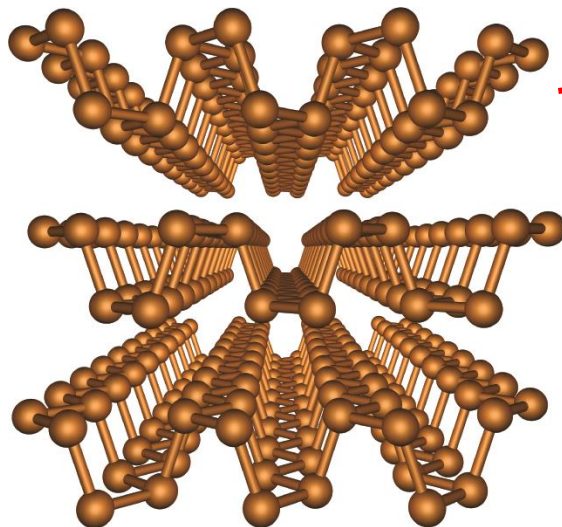
$\alpha$ -Sn ( $Fd-3m$ )  
grey tin



# Group 15 allotropic modifications

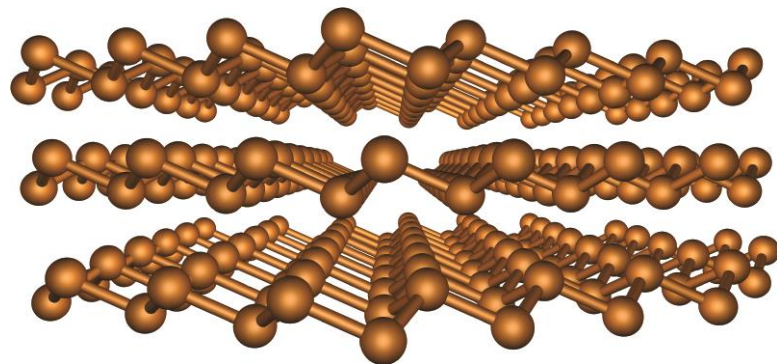


Tetrahedral molecules  
( $P_4$ ,  $As_4$ ,  $Sb_4$ )  
White phosphorus

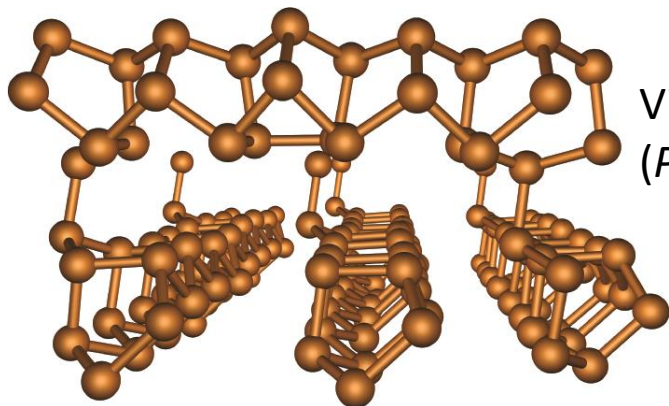


Orthorhombic layered  
structure,  $Cmca$  (P, As)  
Black phosphorus

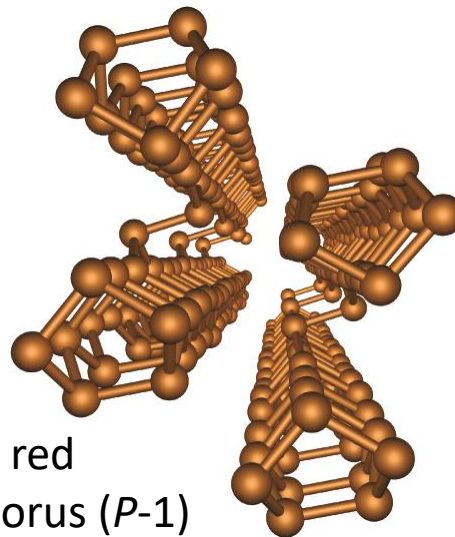
Individual sheets can be cleaved  
-> phosphorene



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



Violet phosphorus  
( $P2/c$ )

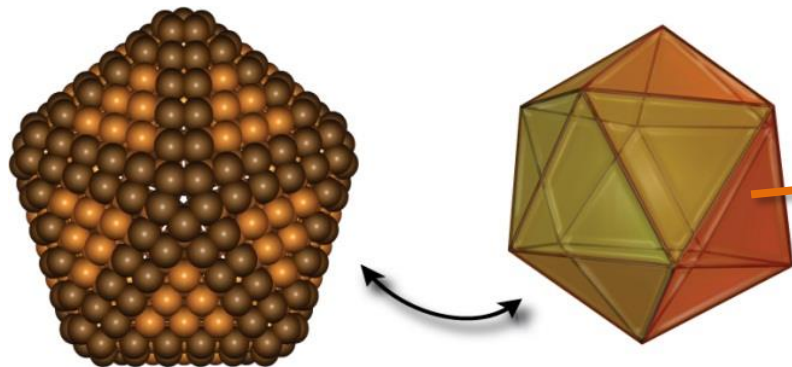


Fibrous red  
phosphorus ( $P-1$ )

# Group 15 nanostructures

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

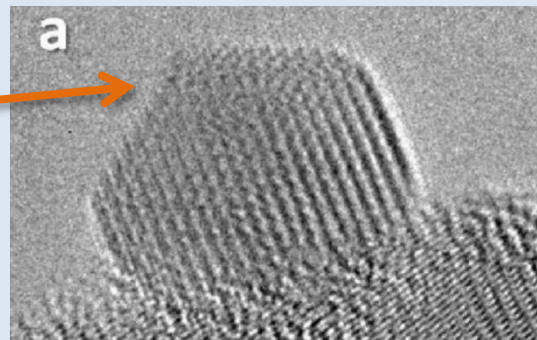
## Polyhedra (e.g. P<sub>180</sub>)



*Chem. Eur. J.* **2007**, *13*, 5232 ([DOI](#))

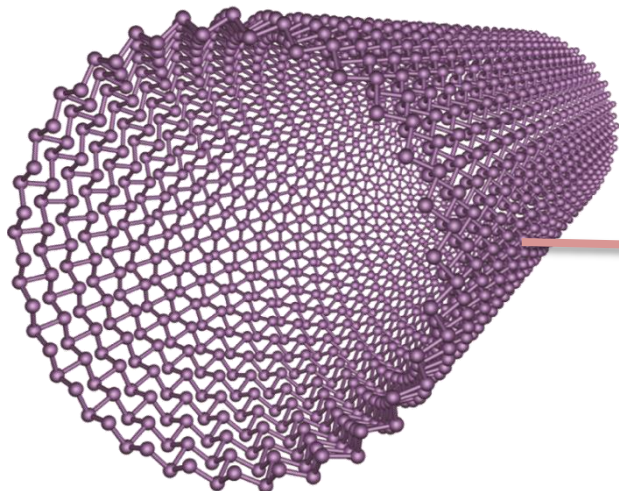
*Theor. Chem. Acc.* **2011**, *129*, 412 ([DOI](#))

## Bismuth nanoicosahedra

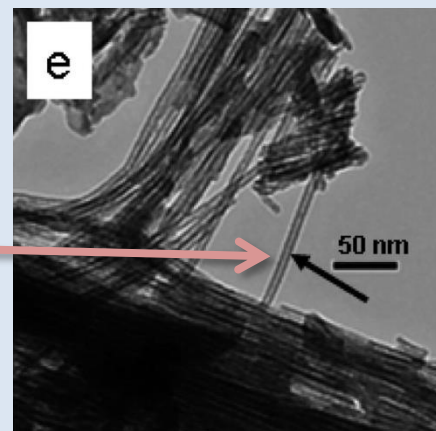


Y. Selzer et al, *Nano Lett.* **2012**, *12*, 1087.

## Nanotubes

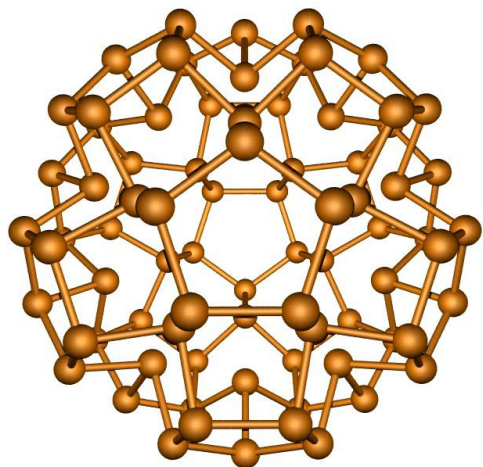


## Bismuth nanotubes

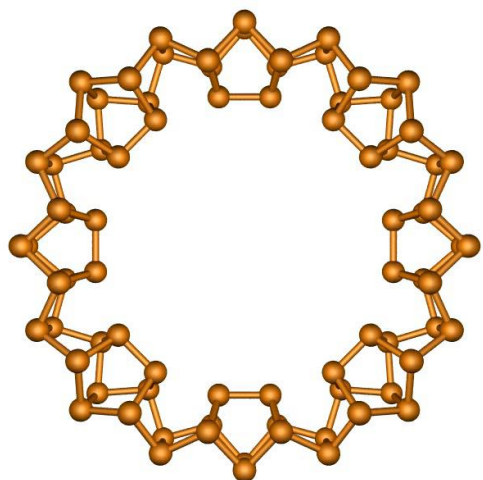


Pfefferle et al, *J. Phys. Chem. C*, **2010**, *114*, 3431.

# Phosphorus nanostructures

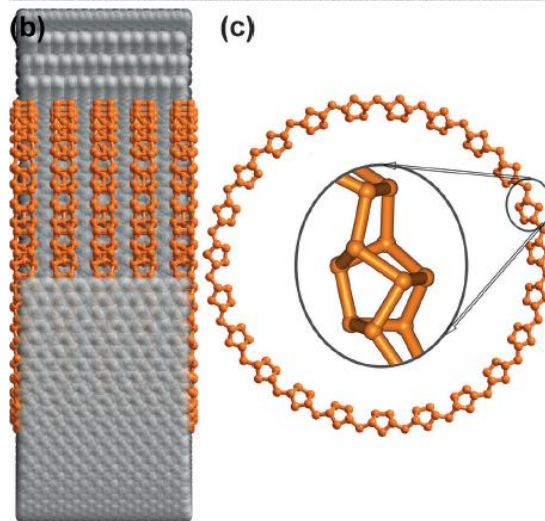
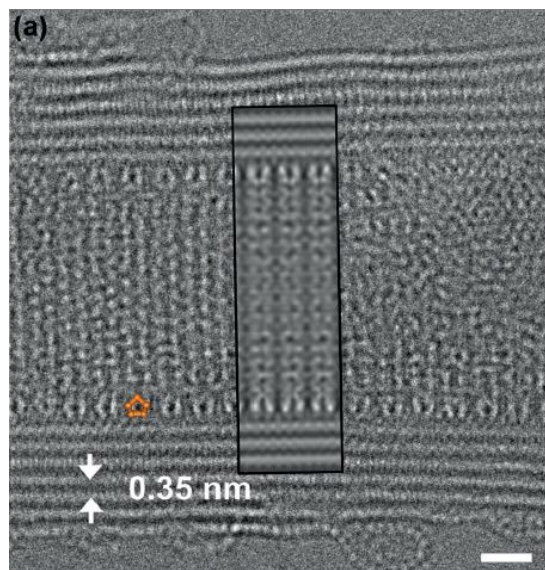


$P_{80}$  fullerene ( $I_h$ )

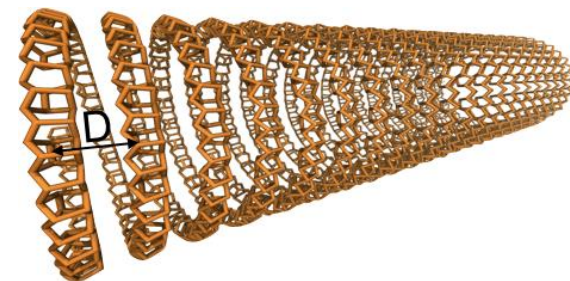


$P_{80}$  ring ( $C_{4v}$ )

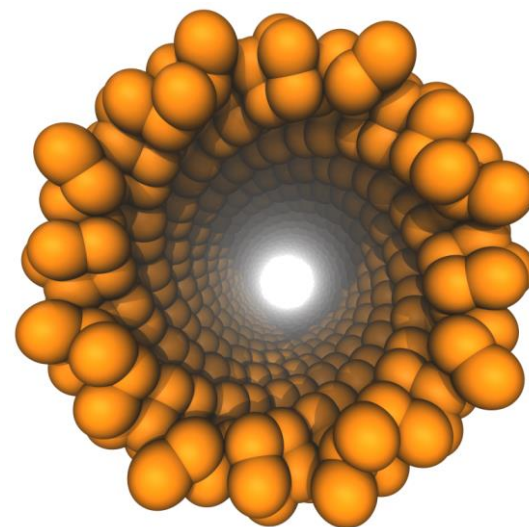
Icosahedral and Ring-shaped Allotropes of Phosphorus  
Karttunen, A. J.; Linnolahti, M.; Pakkanen, T. A.  
*Chem. Eur. J.* **2007**, *13*, 5232–5237 ([DOI](#)).



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



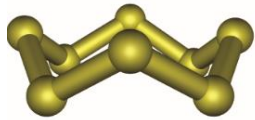
Red phosphorus helices



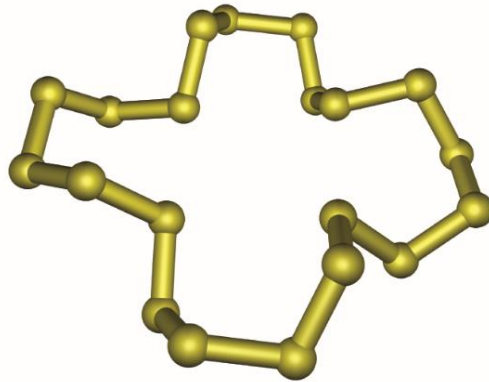
One-dimensional Phosphorus Nanostructures: from  
Nanorings to Nanohelices  
Sansone, G.; Maschio, L.; Karttunen, A. J. *Chem. Eur. J.*  
**2017**, *23*, 15884–15888. ([DOI](#)).

# Group 16 allotropes

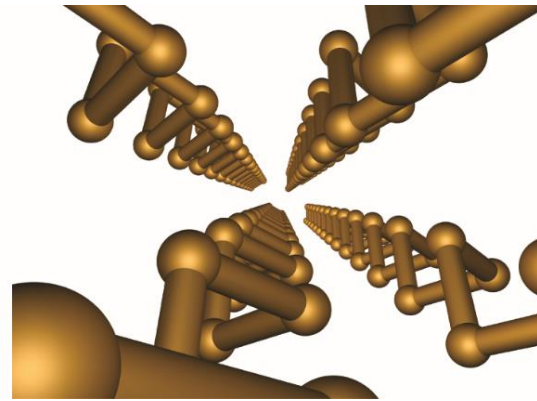
- Whereas the allotropes of group 15 elements are three-coordinate, the additional valence electron of group 16 elements makes their allotropes two-coordinate
- This imposes limits on the capability to form infinite structural networks, but the elemental chemistry of S and Se is still very rich
- The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



$\alpha$ -cyclo-S<sub>8</sub> (*Fddd*)



Cyclo-S<sub>20</sub> (*Pbcn*)



Gray selenium consisting of helical chains (*P3<sub>1</sub>21*)



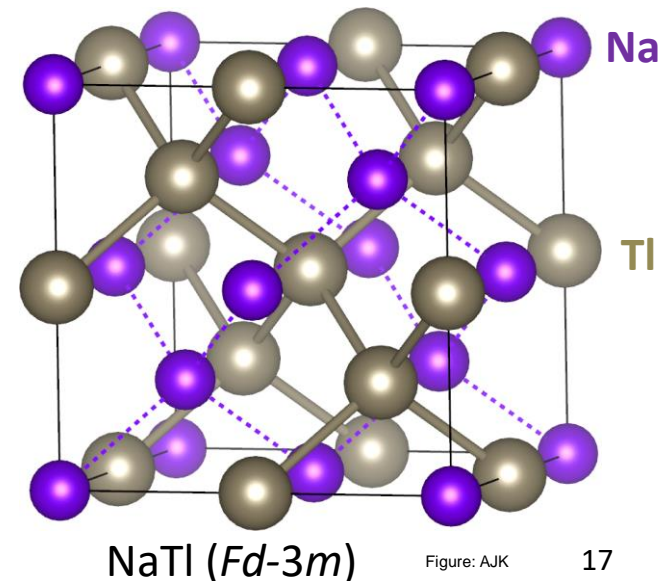
# Zintl phases

- 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**
  - $Tl^-$  ions 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" picture (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

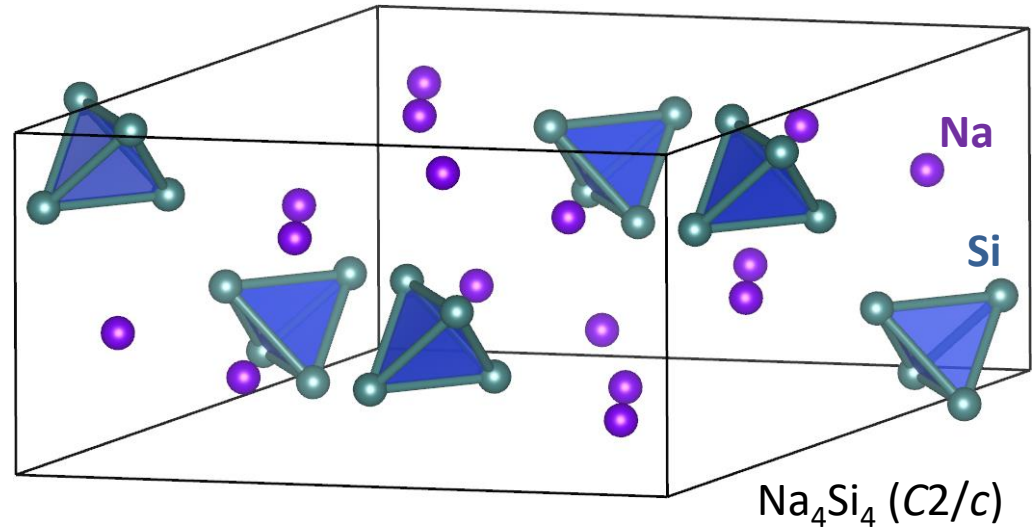
Figure: Wikipedia/AJK



# Examples of Zintl phases (1)

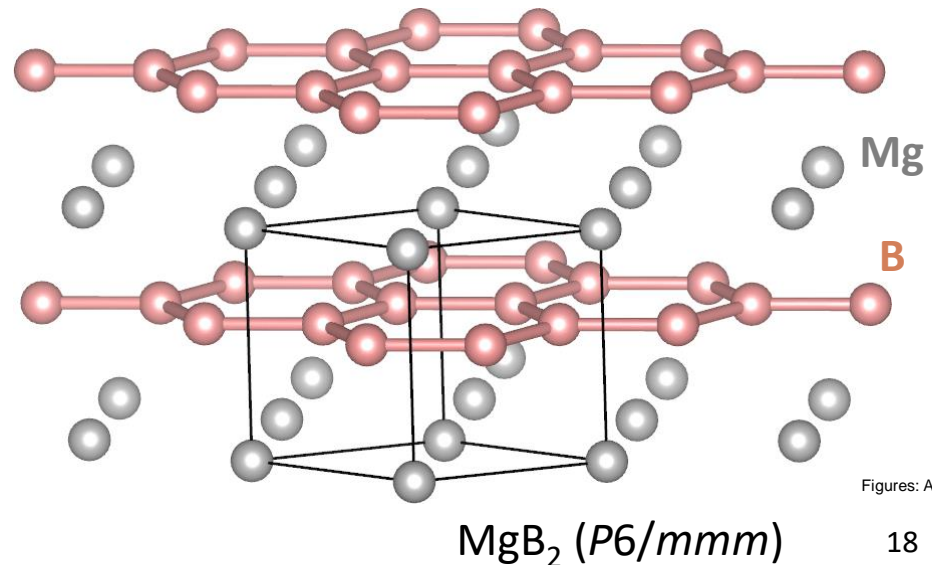
## NaSi ( $\text{Na}_4\text{Si}_4$ )

- Each Na atom donates  $1e^-$
- Each Si atom accepts  $1e^-$
- $[\text{Si}_4]^{4-}$  tetrahedra are isoelectronic with  $\text{P}_4$  tetrahedra (white phosphorus)



## MgB<sub>2</sub>

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

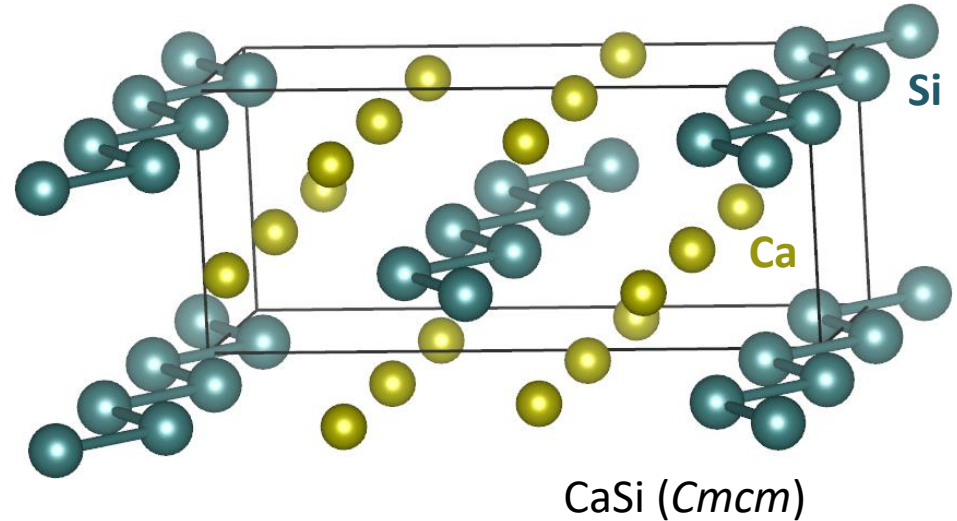


Figures: AJK

# Examples of Zintl phases (2)

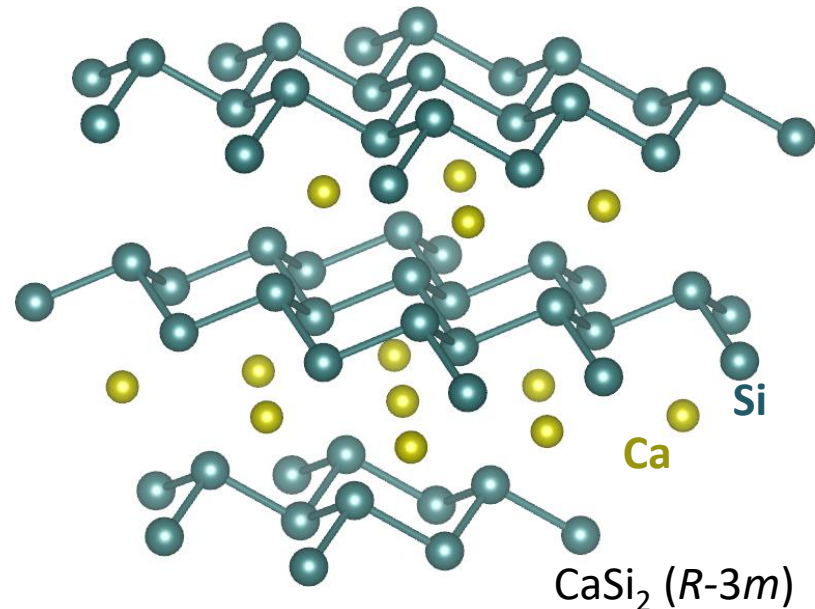
## CaSi

- 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<sub>2</sub>

- 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

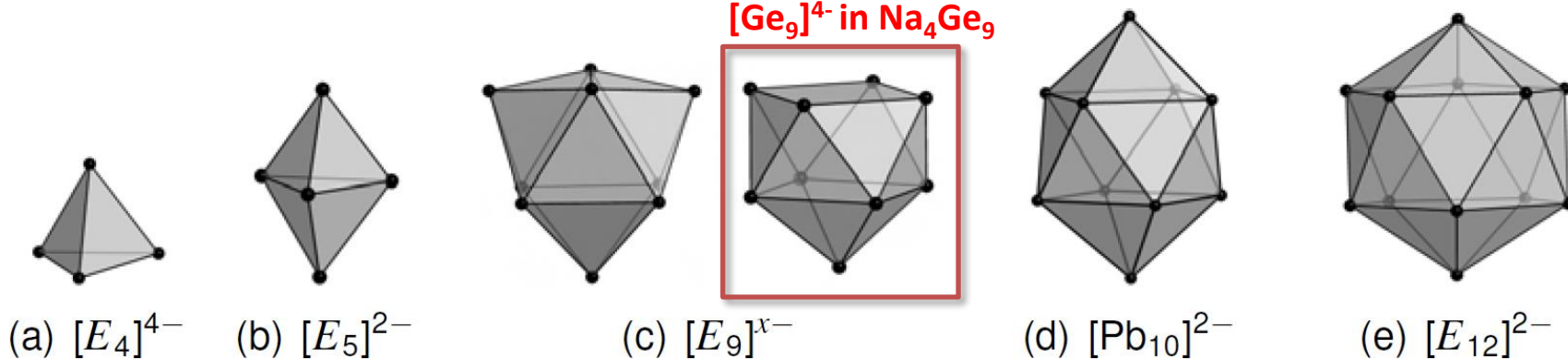


# Group 14 Zintl ions (Si, Ge, Sn, Pb)

Many solid-state Zintl phases contain discrete anions

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

Figure: Sandra Scharfe / [Dissertation](#) 2010 (TUM)



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

**Strained bond angles in comparison to diamond-like bulk  $\alpha\text{-Si}$  /  $\alpha\text{-Ge}$  /  $\alpha\text{-Sn}$  with  $109.5^\circ$  angles**

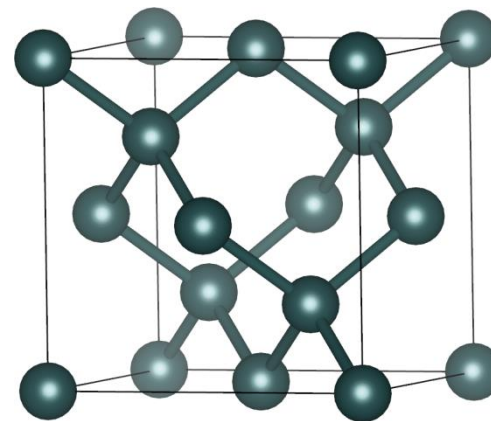
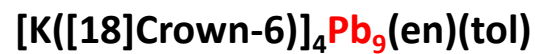
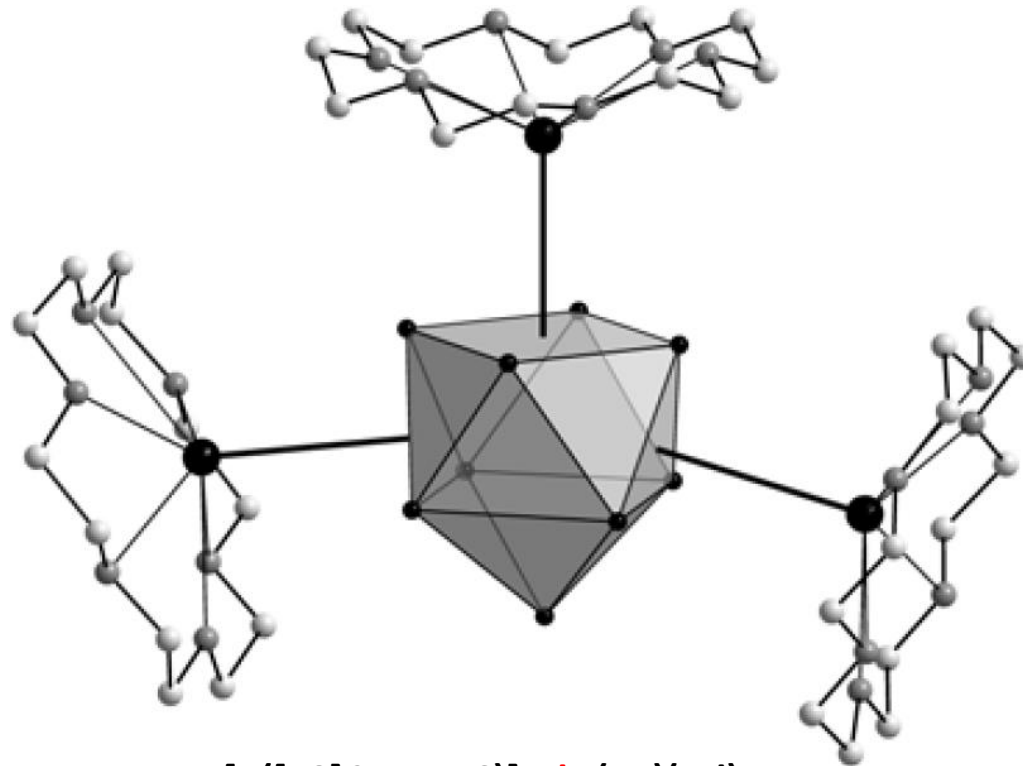


Figure: AJK

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



S. Scharfe, [Dissertation](#), Technical University of Munich, 2010

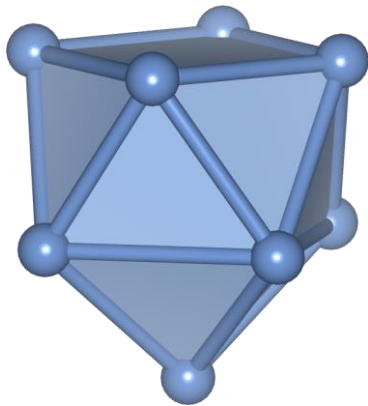
# Zintl phases as precursors for preparing novel materials

NATURE|Vol 443|21 September 2006

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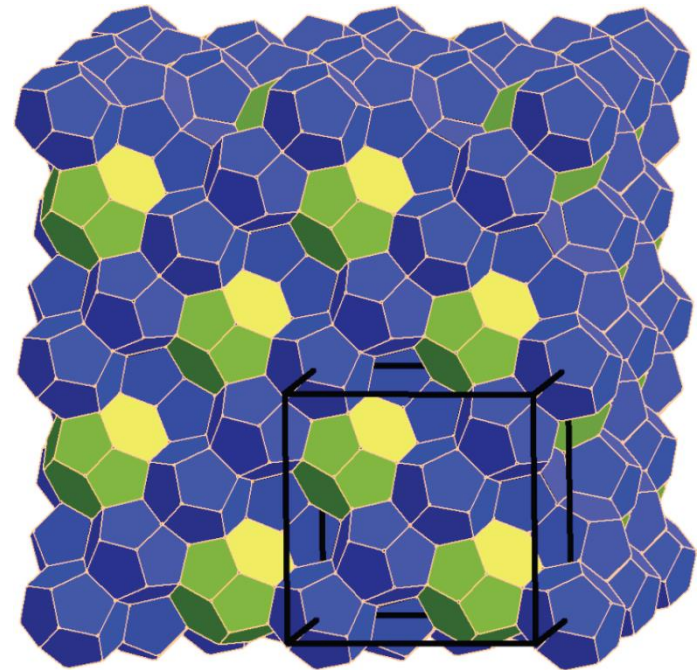
## A guest-free germanium clathrate

Arnold M. Guloy<sup>1,2</sup>, Reiner Ramlau<sup>1</sup>, Zhongjia Tang<sup>1,2</sup>, Walter Schnelle<sup>1</sup>, Michael Baitinger<sup>1</sup> & Yuri Grin<sup>1</sup>



$[\text{Ge}_9]^{4-}$  (in  $\text{Na}_4\text{Ge}_9$ )

*Mild oxidation in  
ionic liquid*



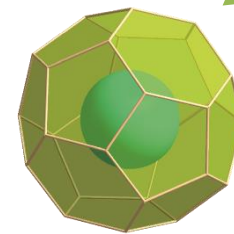
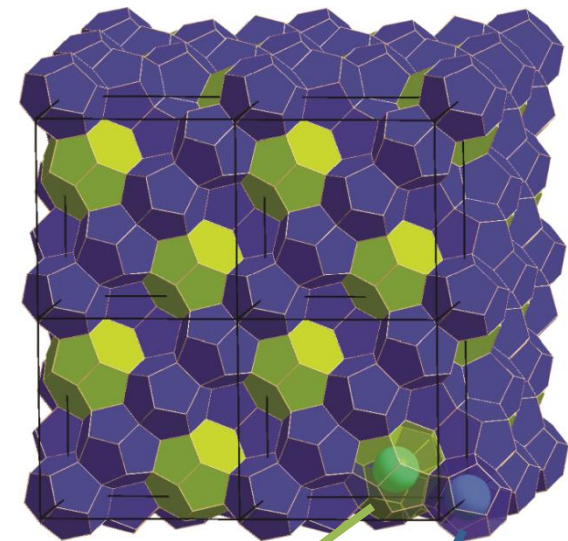
$\text{Ge}_{136}$  Clathrate-II (*cF136*)

# Zintl phases:

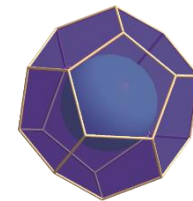
## Semiconducting group 14 clathrates (1)

- 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<sup>1</sup>
  - Low lattice thermal conductivity.
  - Semiconductors: electronic properties can be tuned by controlled doping.

Clathrate-II ( $Fd-3m$ )



$M_{28}$  cage



$M_{20}$  cage

( $M = \text{Si, Ge, Sn}$ )

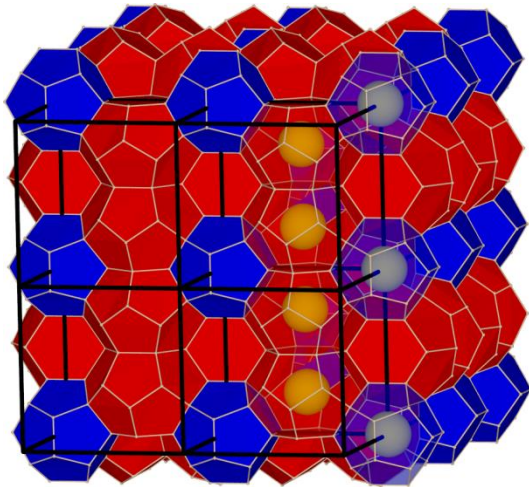
<sup>1</sup> G. S. Nolas et al. *Phys. Rev. Lett.*, **1999**, 82, 779.  
G. S. Nolas et al. *J. Mater. Chem.*, **2008**, 18, 842.  
B. B. Iversen et al. *Dalton Trans.*, **2010**, 39, 978.

# 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  $\text{Na}_{24}\text{Si}_{136}$  are also known
- **The atomic composition and properties are somewhat tunable**

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



- $\text{Ba}_8[\text{Ga}_{16}\text{Ge}_{30}]$  (**anionic** framework)
- Each Ba atom donates  $2e^-$
- Ga atoms have  $1e^-$  less than Ge, so the 4-coordinated framework needs  $16e^-$

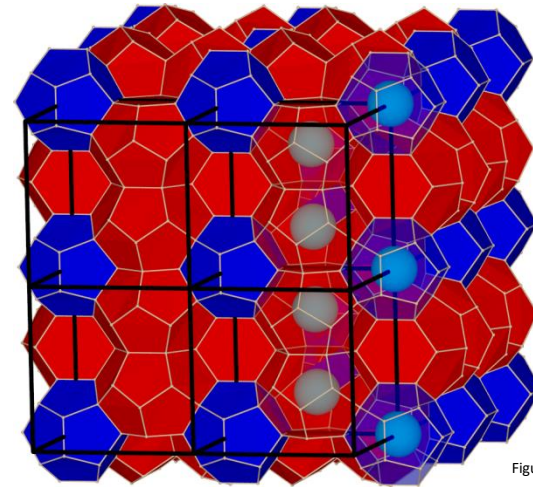


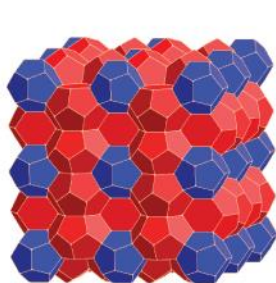
Figure: AJK

- $\text{I}_8[\text{As}_8\text{Ge}_{38}]$  (**cationic** framework!)
- Each I atom accepts  $1e^-$
- As atoms have  $1e^-$  more than Ge, these extra electrons are donated to the I atoms

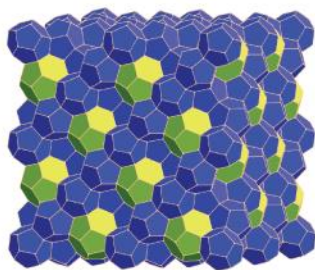


# Examples of clathrate frameworks

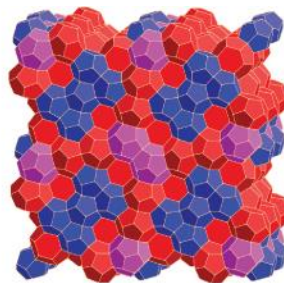
Very rich structural chemistry (all frameworks are not yet known for group 14 clathrates)



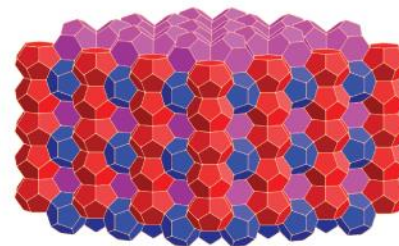
I ( $Pm-3n$ )



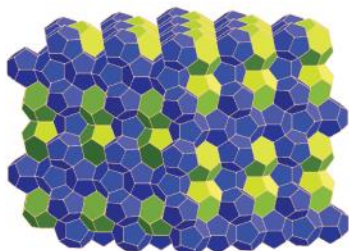
II ( $Fd-3m$ )



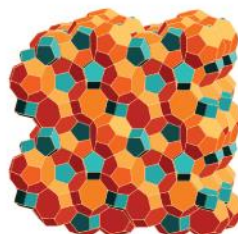
III ( $P4_2/mnm$ )



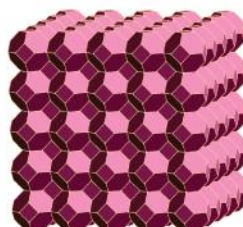
IV ( $P6/mmm$ )



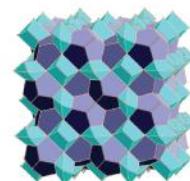
V ( $P6_3/mmc$ )



VI ( $I-43d$ )



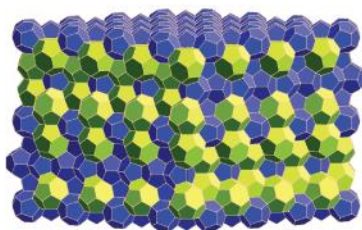
VII ( $Im-3m$ )



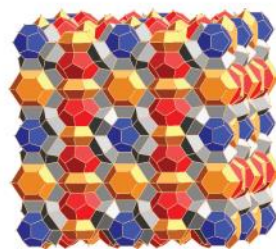
VIII ( $I-43m$ )



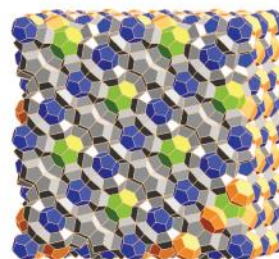
H ( $P6/mmm$ )



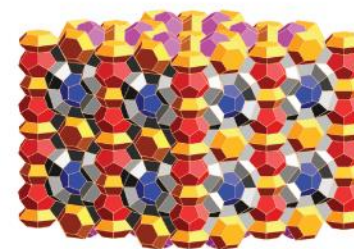
"II-4H" ( $P6_3/mmc$ )



I-100 ( $Pm-3n$ )



II-100 ( $Fd-3m$ )



IV-100 ( $P6/mmm$ )

# Currently known group 14 clathrates

1												18					
H													He				
2												13	14	15	16	17	
Li	Be											B	C	N	O	F	Ne
3												13	14	15	16	17	
Na	Mg																
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	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		

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
$\text{Na}_8[\text{Si}_{46}]$	$\text{K}_8[\text{Al}_8\text{Ge}_{38}]$	$\text{I}_8[\text{Ge}_{38}\text{P}_8]$	$\text{K}_{1.6}\text{Cs}_{6.4}[\text{Sn}_{44}\square_2]$
$\text{Na}_{8-x}\text{Ba}_x[\text{Si}_{46}]$	$\text{Rb}_8[\text{Al}_8\text{Ge}_{38}]$	$\text{Br}_8[\text{Ge}_{38}\text{P}_8]$	$\text{Rb}_8[\text{Sn}_{44.6}\square_{1.4}]$
$\text{Na}_x\text{Ba}_6[\text{Si}_{46}]$	$\text{K}_8[\text{Ga}_8\text{Ge}_{38}]$	$\text{Cl}_8[\text{Ge}_{38}\text{P}_8]$	$\text{Cs}_8[\text{Sn}_{44}\square_2]$
$\text{K}_{7.62}\square_{0.38}[\text{Si}_{46}]$	$\text{Rb}_8[\text{Ga}_8\text{Ge}_{38}]$	$\text{I}_8[\text{Ge}_{38}\text{As}_8]$	$\text{K}_8[\text{Al}_8\text{Sn}_{38}]$
$\text{Rb}_{6.15}\square_{1.85}[\text{Si}_{46}]$	$\text{Cs}_8[\text{Ga}_8\text{Ge}_{38}]$	$\text{Br}_8[\text{Ge}_{38}\text{As}_8]$	$\text{Rb}_8[\text{Al}_8\text{Sn}_{38}]$
$\text{K}_8[\text{Ga}_8\text{Si}_{38}]$	$\text{K}_8[\text{In}_8\text{Ge}_{38}]$	$\text{Cl}_8[\text{Ge}_{38}\text{As}_8]$	$\text{K}_8[\text{Ga}_8\text{Sn}_{38}]$
$\text{Rb}_8[\text{Al}_8\text{Si}_{38}]$	$\text{Rb}_8[\text{In}_8\text{Ge}_{38}]$	$\text{I}_8[\text{Ge}_{38}\text{Sb}_8]$	$\text{Rb}_8[\text{Ga}_8\text{Sn}_{38}]$
$\text{Rb}_8[\text{Ga}_8\text{Si}_{38}]$	$\text{Cs}_8[\text{In}_8\text{Ge}_{38}]$	$\text{Br}_8[\text{Ge}_{38}\text{Sb}_8]$	$\text{Cs}_8[\text{Ga}_8\text{Sn}_{38}]$
		$\text{I}_8[\text{Ge}_{14}\text{Ga}_{12}\text{Sb}_{20}]$	$\text{Cs}_8[\text{Zn}_4\text{Sn}_{42}]$
			$\text{Cs}_8[\text{Cd}_4\text{Sn}_{42}]$