TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Wed	07.09.	Course Introduction & Short Review of the Elements
2.	Fri	09.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Mon	12.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Fri	16.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Mon	19.09.	Transition Metals: General Aspects & Pigments
6.	Wed	21.09.	Redox Chemistry
7.	Fri	23.09.	Crystal Field Theory (Linda Sederholm)
8.	Mon	26.09.	V, Nb, Ta & Metal Complexes & MOFs
9.	Wed	28.09.	Cr, Mo, W & 2D materials
10.	Fri	30.09.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
10.	Mon	03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
11.	Fri	07.10.	Lanthanoids + Actinoids & Luminescence
12.	Mon	10.10.	EXTRA
14.	Wed	12.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
15.	Fri	14.10.	Inorganic Materials Chemistry Research

EXAM: Oct. 18, 9:00-12:00

INSTRUCTIONS for SEMINAR PRESENTATIONS

- Presentation (~20 min) is given in a group of (two or) three persons
- It is evaluated in the scale: 15 ~ 25 points
- Presentation is given in English, and the slides are put up in MyCourses afterwards
- Content of the presentation:

  - **ELEMENT:** discovery, origin of name, abundancy, world production, special features if any, etc.

  - **CHEMISTRY:** position in Periodic Table, electronic configuration, oxidation states, metal and ionic sizes, reactivity, etc.

  - **COMPOUNDS:** examples of important compounds, their properties and applications, etc.

  - **SPECIFIC FUNCTIONALITIES/APPLICATIONS:** Two or three examples of exciting functionalities/applications of the element or its compounds. <u>Here the meaning is to discuss why this specific element is needed in each selected application.</u> You will be given one scientific article for a reference, and you should search for couple of more (recent) articles to be discussed in the presentation.

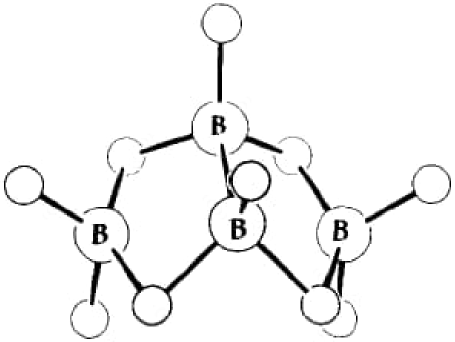
PRESENTATION TOPICS/SCHEDULE

Fri	16.09.	Ti: Mäki & Israr
		Zn: Rautakorpi, Stenbrink & Hyvärinen
Mon	26.09.	Nb: Sousa, Rahikka & Tong
Wed	28.09.	Mo: Alimbekova
Fri	30.09.	Mn: Tao & Song (Zonghang)
		Cu: Marechal, Weppe & Ishtiaq
		Ru: Järvinen & Verkama
Fri	07.10.	Eu: Bardiau, Wolfsberger & Klingerhöfer
		Nd: Helminen
		U: Airas & Holopainen
Wed	12.10.	Co: Song (Yutong) & Wang
		In: Antila & Wallius
		Te: Peussa & Heylen

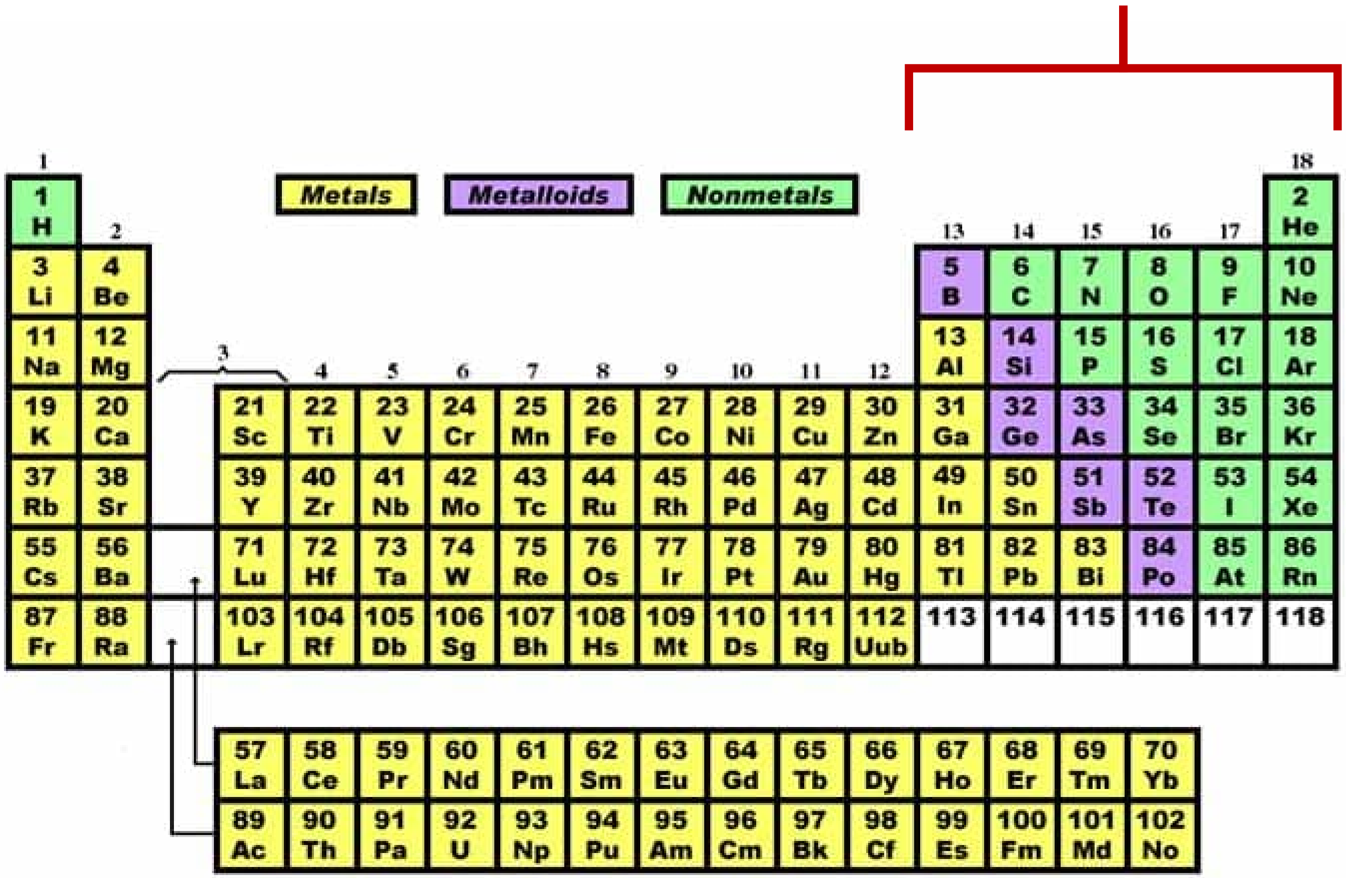
QUESTIONS: Lecture 3

Name your file Exe-3-Familyname; Return by noon tomorrow into MyCourses drop-box

1. **Each of the following main group elements is specific/unique among all the elements, regarding at least one chemical or physical feature: B, F, He. Explain which feature.**
2. **For a hypothetical group of elements (Aa – Ff) in Periodic Table, the following melting points have been reported: Aa 30 °C, Bb 100 °C, Cc 400 °C, Dd 550 °C, Ee 500 °C, Ff 250 °C. Based on this information, predict (with short explanations) the metallic versus non-metallic nature of each element. When combined with OH groups, do you expect Bb to form acidic or basic compound?**
3. **Name the following boron compound, list the types of bonds it has, and draw the so-called semitopological diagram for it: B_4H_{10}**



TODAY



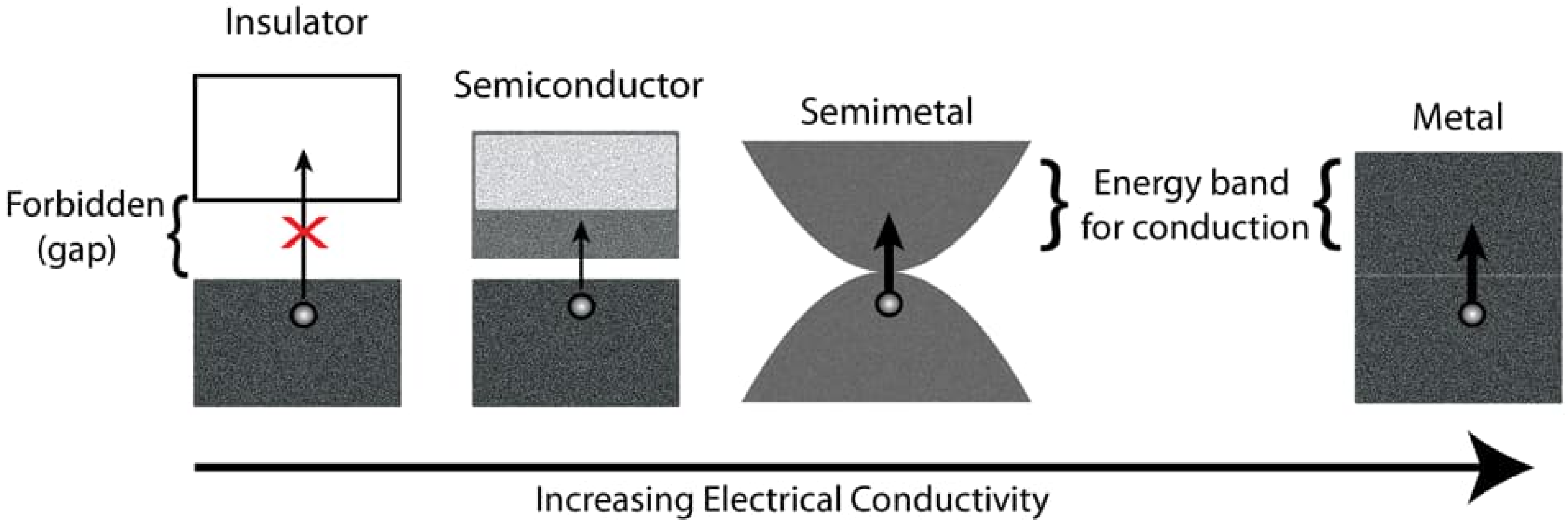
Metals | Metalloids | Nonmetals

1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																		2 He
3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113	114	115	116	117	118

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Metalloids

- Metalloid: Element with properties intermediate between those of typical metals and nonmetals
- Metalloids: boron, silicon, germanium, arsenic, antimony, tellurium & polonium
- Naming in 1950s: *metalloid* (original meaning: metalloid = nonmetal)
- Sometimes: metalloid ≈ semimetal (in physics to refer to the band structure)
- Semimetal should not be confused with semiconductor (or halfmetal)
- Metalloids typically: brittle and somewhat shiny solids, important industrial materials (e.g. transistors, other semiconductor devices, ceramics, solar cells)

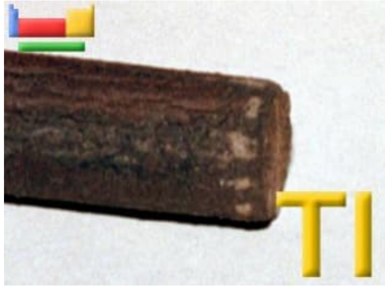


When going from metals to non-metals (from left to right in Periodic Table):
A gradual change in acid-base character (seen for the OH compounds)

- In compounds with OH groups (E-O-H) electronegativity of the cation (E) defines whether the compound is an oxoacid or a base
- small electronegativity: $E\text{-}O\text{-}H \rightarrow E^+ + OH^-$ (base)
- large electronegativity: $E\text{-}O\text{-}H \rightarrow E\text{-}O^- + H^+$ (acid)
- For example: elements of the third period:

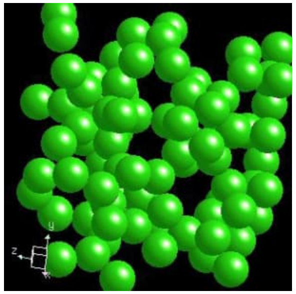
NaOH	strong base
$Mg(OH)_2$	base
$Al(OH)_3$	amfolyte
$Si(OH)_4$	weak acid [H_4SiO_4]
$OP(OH)_3$	acid [H_3PO_4]
$O_2S(OH)_2$	strong acid [H_2SO_4]
$O_3Cl(OH)$	strong acid [$HClO_4$]

Electro-negativity increases



BORON GROUP: MELTING POINTS

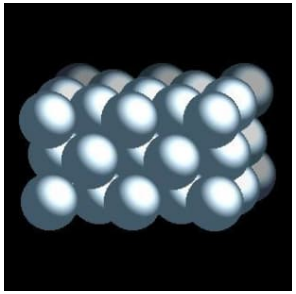
2180 °C



Boron

Rhombohedral

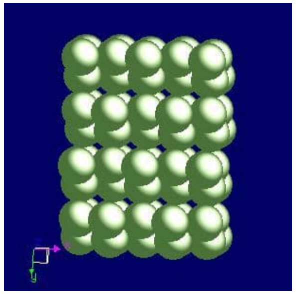
660 °C



Aluminum

CCP

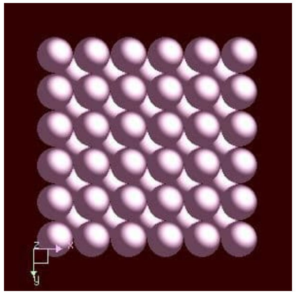
30 °C



Gallium

Orthorhombic

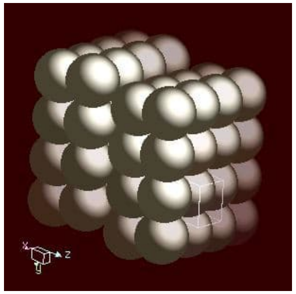
157 °C



Indium

Tetragonal

303 °C



Thallium

HCP

BORON: ELECTRON DEFICIENT COMPOUNDS

- **B: $1s^2 2s^2 2p^1$**

  3 valence electrons → octet not possible with covalent bonds

  electronegativity 2.0 → ionic bonds not possible

- **Difficult to achieve electron octet → *electron deficient* compounds**
- **Hydrogen compounds of boron, boranes, are typical examples of electron deficient compounds**
- **Also Al, Ga, Be and Li form electron deficient compounds:**

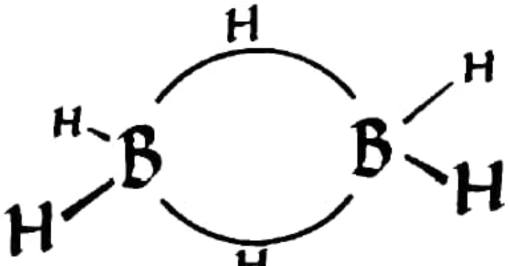
  $(AlH_3)_n$, $Al_2(CH_3)_6$, $[Be(CH_3)_2]_n$, $[Li(CH_3)]_4$
- **Normal single bond: 2 atoms and 2 bond electrons (2c-2e)**
- **Electron deficient compound: 3 atoms and 2 bond electrons (3c-2e)**

BORANES

- B_nH_{n+4} or B_nH_{n+6} ($n = 2 - 20$)
- First synthesized by Alfred Stock 1909:
  $MgB_2 + HCl \rightarrow B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_{10}H_{14}, \ldots$
- Air-sensitive compounds
  → closed system, inert synthesis atmosphere
- Naming:
  number of B atoms with prefix,
  number of H atoms in parenthesis at the end,
  e.g. B_2H_6 diborane(6), B_4H_{10} tetraborane(10), B_5H_9 pentaborane(9)
- (3c-2e) weak bond → breaking the bond requires little energy
  B-O bond strong → formation releases lot of energy
  → burning of boranes is strongly exothermic
  (1950s boranes were investigated as “superfuels” in aircrafts and spaceships)

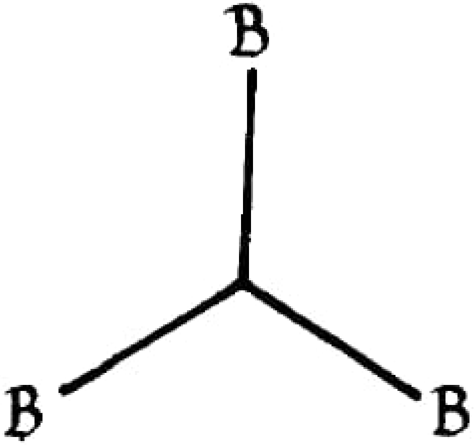
SEMITOPOLOGICAL DIAGRAMS

- **William Lipscomb (Nobel 1976)**
- **Bonds:** **B-H (terminal 2c-2e)**
  B-H-B (3c-2e)
  B-B (2c-2e)
  B-B-B (3c-2e)

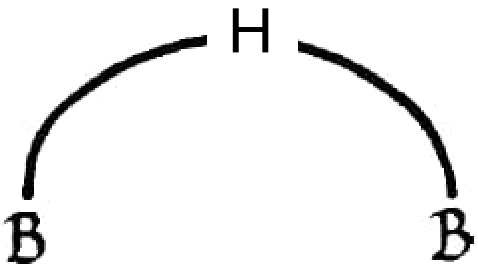


B_2H_6

2-center

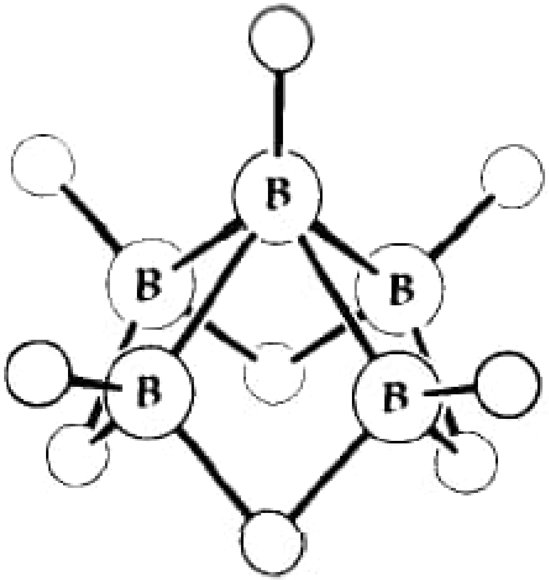


3-center central



3-center open

EXAMPLE: B_5H_9

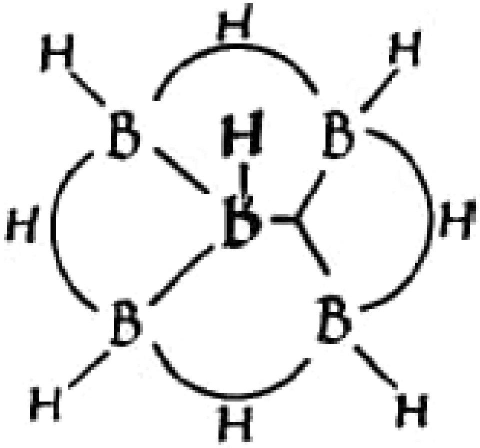


Valence electrons:

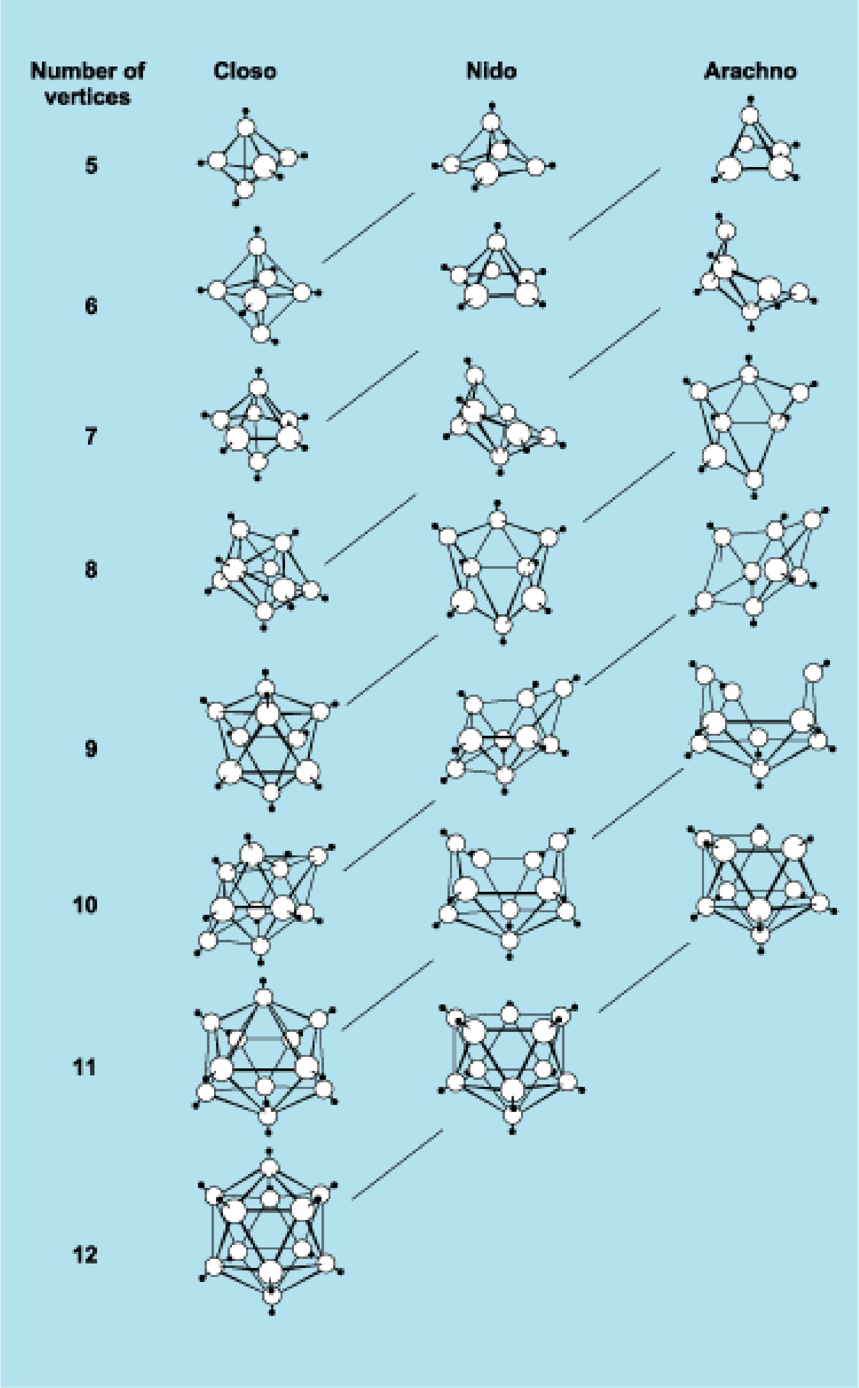
5 x 3e + 9 e = 24 e

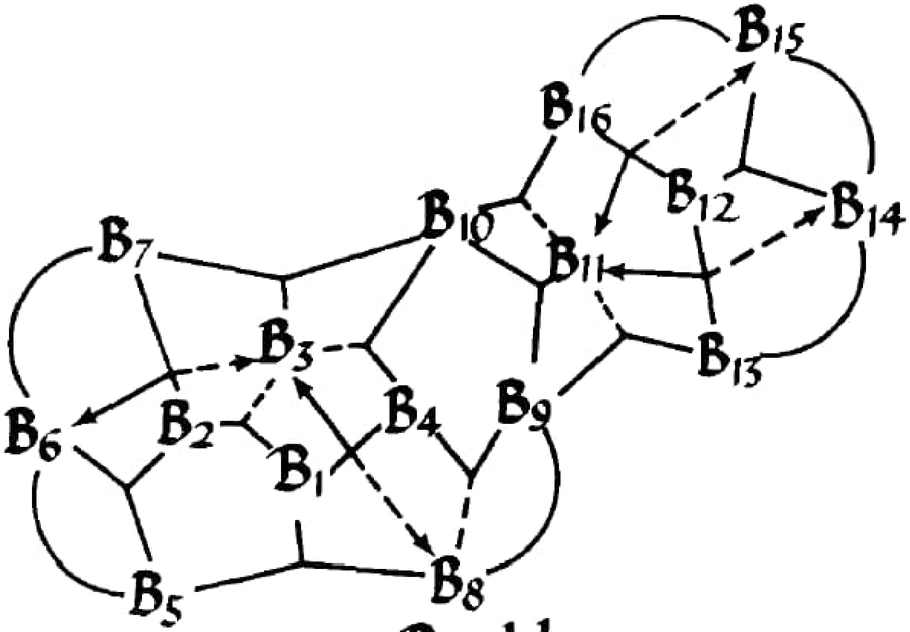
Bonds:

5	**2c-2e**	**B-H**	**10 e**
4	**3c-2e**	**B-H-B**	**8 e**
2	**2c-2e**	**B-B**	**4 e**
1	**3c-2e**	**B-B-B**	**2 e**



B_5H_9


Number of vertices
Closo
Nido
Arachno
5
6
7
8
9
10
11
12


B15
B16
B12
B14
B10
B11
B7
B13
B3
B4
B9
B6
B2
B1
B5
B8

$B_{16}H_{20}$

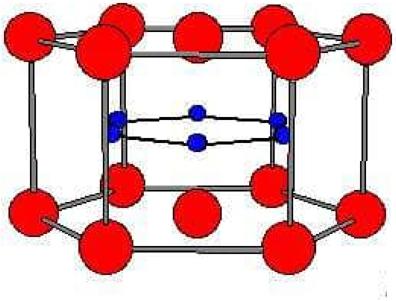
BORIDES

- Binary compounds of boron with metals
  - more than 200 different compounds
  - stoichiometry varies M_5B … MB_{66} (e.g. M_2B, MB, MB_2, MB_4, MB_6)
  - M-rich typical for *d*-block transition metals, B-rich for main group metals, lanthanoids and actinoids
  - known are also nonstoichiometric and mixed borides
  - extremely hard, high-temperature resistive, chemically inert
  - uses: coatings, electrodes, nuclear technology (protection, neutron counter: $^1n + {}^{10}B \rightarrow {}^7Li + {}^4He$)
- Boron carbide
  - "B_4C" = $B_{12}C_3$
  - one of the hardest materials
  - uses: armor material, bycycles

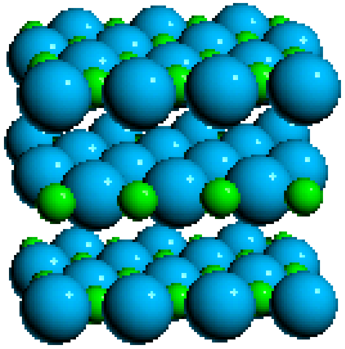
BORIDE STRUCTURES

- **M-rich:**
  - (1) separate B atoms
  - (2) separate B_2 atom pairs
  - (3) B_n chains
  - (4) double chains
  - (5) planes (MB_2)

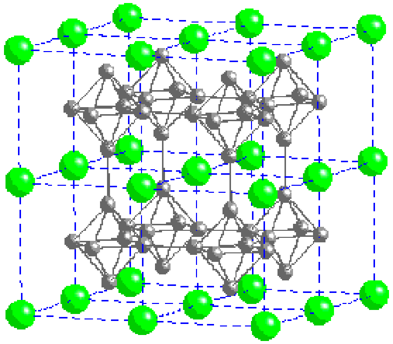
  (catenation tendency of B atoms increases with increasing B content)
- **B-rich:**
  - (1) planes
  - (2) 3D nets
  - (3) clusters (e.g. B_6 octahedra and B_{12} icosahedra)



MgB_2



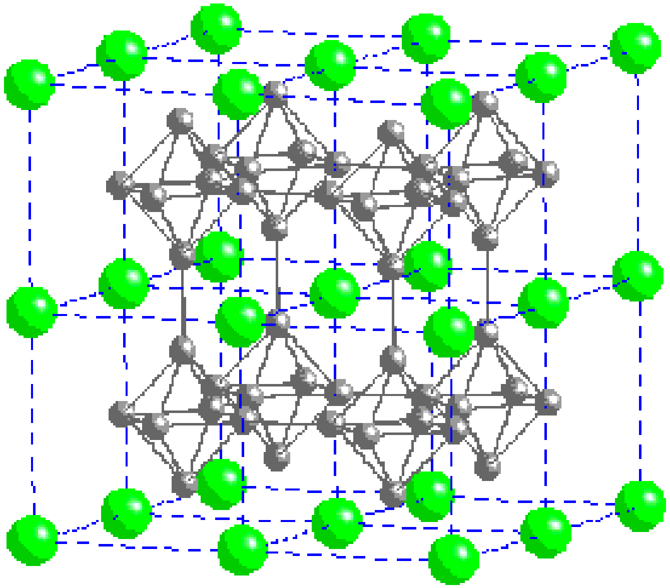
TiB_2



LaB_6

BONDING in BORIDES

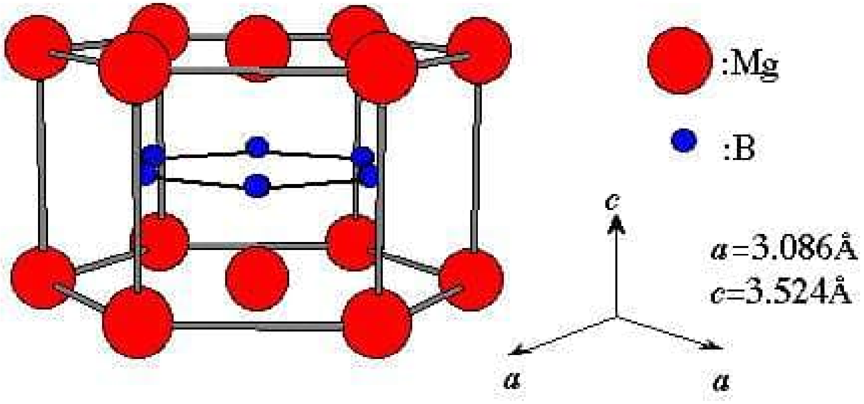
- The simple ionic / covalent / metal bond concepts fail
- **LaB_6:**
  - in B_6 clusters electron-deficient (multicenter-2e) bonds
  - between clusters covalent (2c-2e) B-B bonds
  - move of two electrons from La to B_6 cluster
    → La^{2+}-B_6^{2-} ionic bond
  - third valence electron of La is delocalized (metal bond)
    → good electrical conductivity, good electron emission
    → use: electron guns in electron microscopes

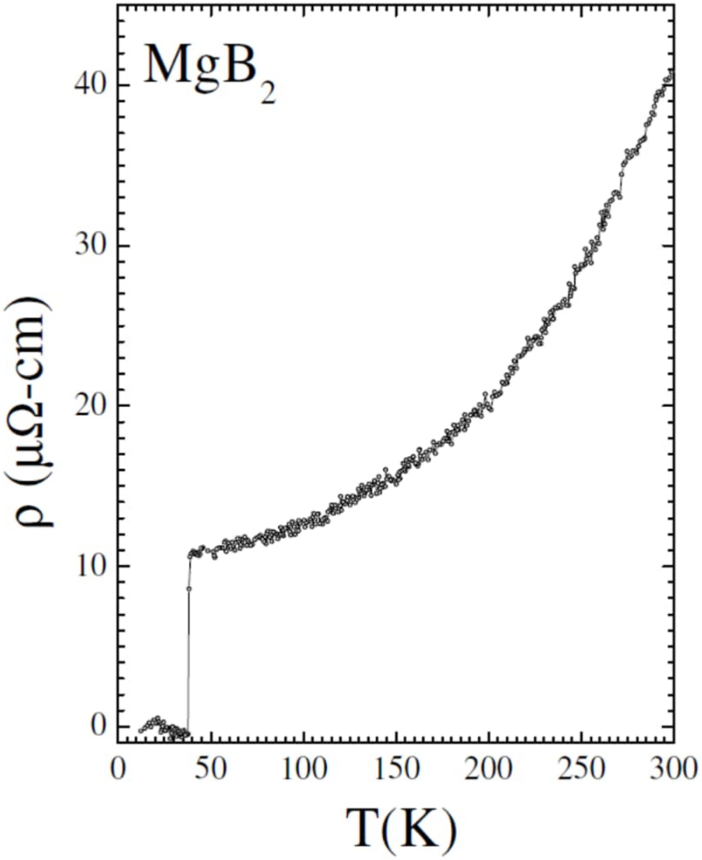


Akimitsu 2001:

Superconductivity with T_c = 39 K

Akimitsu_fig2





BORON-NEUTRON-CAPTURE-THERAPY (BNCT)

- **Treatment of inoperable brain tumors/cancer**
- **Boron (^{10}B) absorbs efficiently neutrons (large absorption cross section)**

  → radioactive ^{11}B:a
- **Radioactive radiation destroys tumor cells**
- **Challenge: to deliver high concentrations of a boron compound specifically to tumor cells**
- **Some boron compounds such as $(B_{12}H_{11}SH)^{2-}$ ion based ones have a tendency to accumulate in cancer cells**

$$\boxed{{}^{10}\mathrm{B} + {}^{1}n \rightarrow {}^{11}\mathrm{B} \rightarrow {}^{7}\mathrm{Li} + {}^{4}\mathrm{He}}$$

Isotope	Hydrogen-1	Boron-10	Carbon-12	Nitrogen-14	Oxygen-16
Neutron-abs. cross-section (barn)	0.33	3.8×10^{3}	3.4×10^{-3}	1.8	1.8×10^{-4}

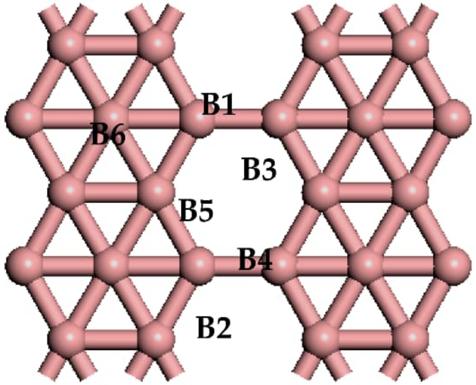
1 barn = 10^{-24} cm^{2}

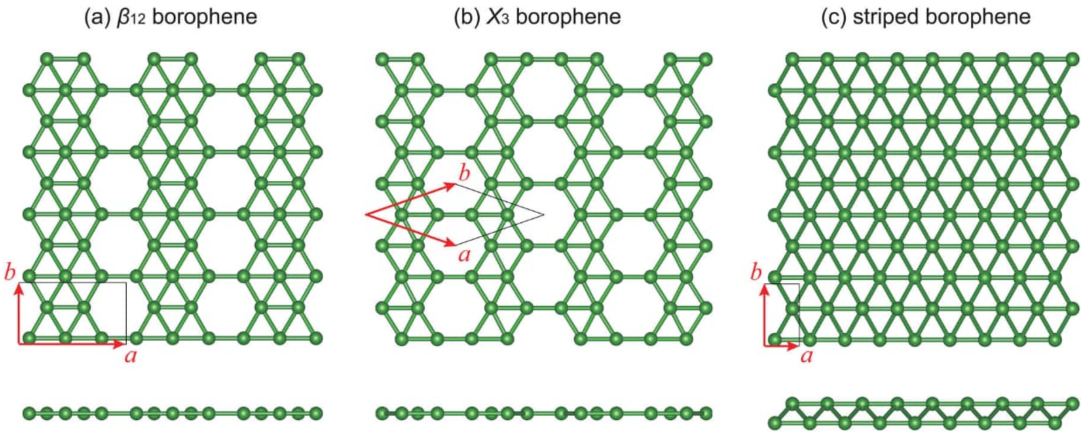
Graphene

Geim & Novoselov (Univ. Manchester) 2004; Nobel (physics) 2010

Borophene

- 2D structure of boron atom sheets
- two-center and multi-center in-plane bonds
- characteristic buckled or crinkled surface
- in nano-scale B and C very similar,
  even though macroscopic allotropes quite different !
- predicted 1997, synthesized by MBE (on Ag) 2015
- bonded weakly to the silver substrate
- metallic, strong, flexible, highly conducting




(a) β_{12} borophene

(b) X_3 borophene

(c) striped borophene

I. Boustani, New quasi-planar surfaces of bare boron, Surface Science 370, 355 (1997).

A.J. Mannix, et al., Synthesis of borophenes: anisotropic, two-dimensional boron polymorphs, Science 350, 1513 (2015).

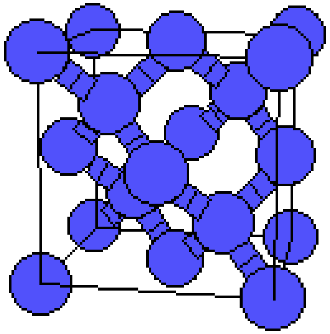
B. Feng, et al., Experimental realization of two-dimensional boron sheets, Nature Chemistry 8, 563 (2016).

ISOELECTRONIC: C-C and B-N

- Boron has one valence electron less and nitrogen one valence electron more than carbon → Boron nitride BN has in average the same number of valence electrons per atom as carbon → C ja BN isoelectronic → resemble each other
- BN forms similar assemblies as those in different carbon allotropes: graphite, diamond, fullerenes, nanotubes and graphene

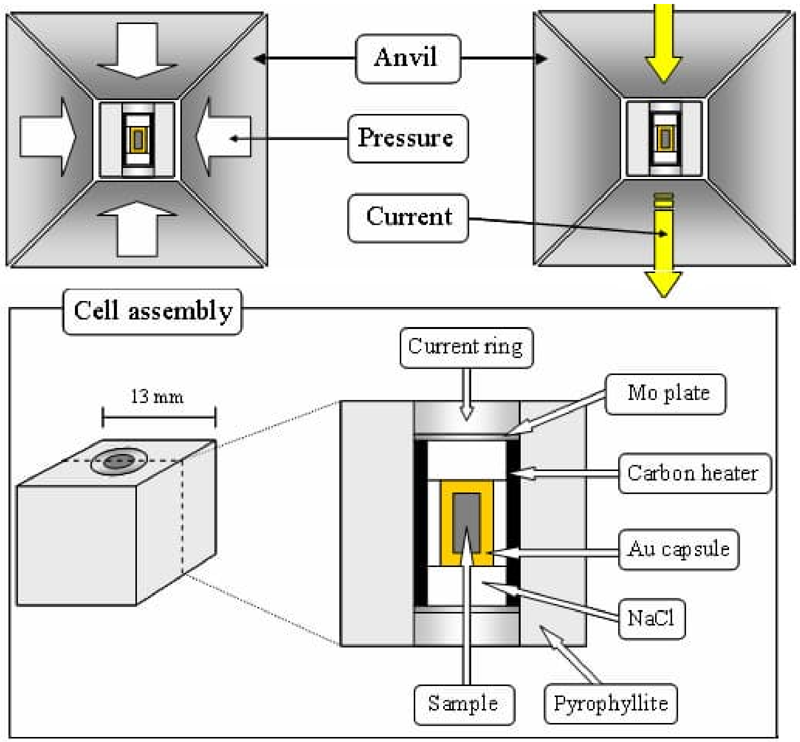
CATENATION in CARBON GROUP

- C-C bond is relatively strong (cf. different carbon allotropes)
- Catenation (= chain-formation capability based on C-C bonds) is characteristic for carbon (ref. organic chemistry) and also typical for the other carbon group elements
- Catenation capability decreases: C > Si > Ge > Sn > Pb
  (after C the next in catenation capability is S)



DIAMOND

- Diamond and graphite known for thousands of years
- The fact that they are different forms of the same element was understood much later
- The critical conbustion experiments were made in the end of 18th century: diamond and graphite produce the same amount of CO_2 (per same mass)
- In nature diamonds have been formed slowly from graphite under high-pressure high-temperature conditions
- The first synthetic diamonds were made in 1953 in Sweden under 7 GPa (= 70 000 atm) and at high temperature using molten Ni as a catalyst (nowadays most of the diamonds are man-made)
- In diamond the C atoms are packed much denser (3.5 g/cm^3) compared to the graphite (2.3 g/cm^3); this is the reason why the high-pressure conditions promotes the formation of diamonds
- For high-tech applications diamond thin films are needed; these are synthesized using hydrocarbons as precursors (methanol, ethanol) (Note: the same tetrahedral *sp*^{3} hybridization as in diamond)

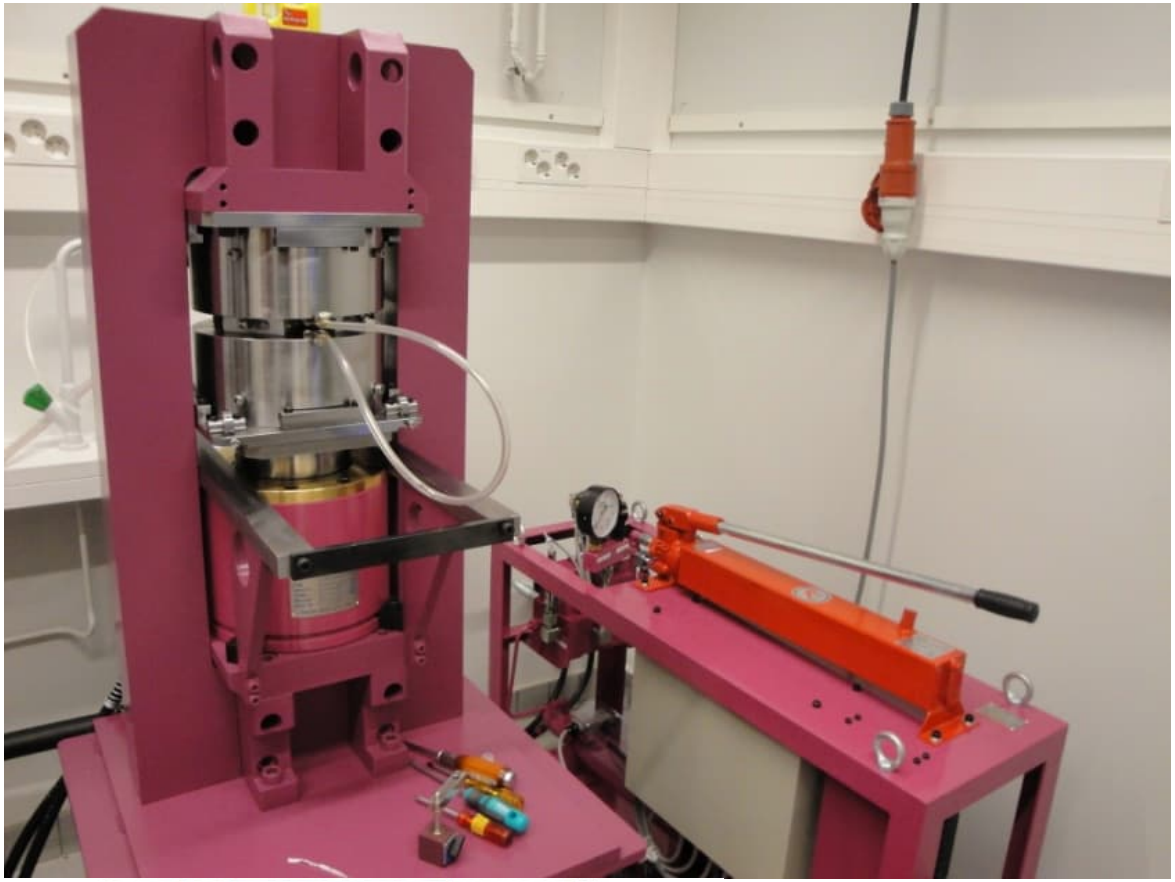


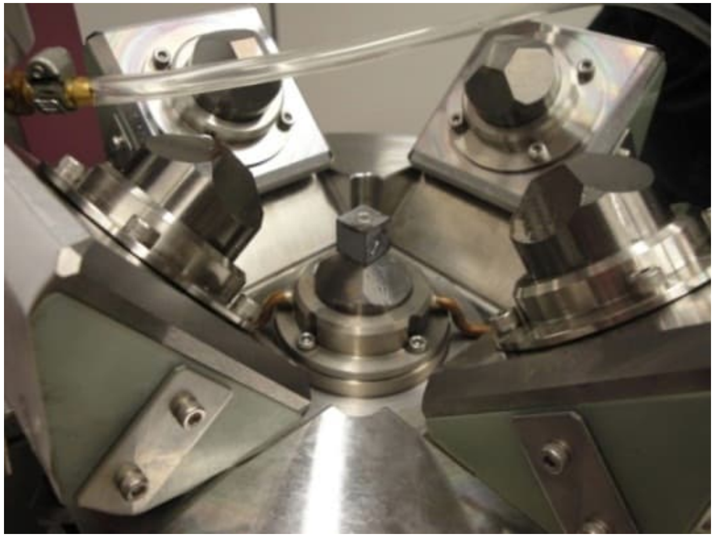
HIGH-PRESSURE SYNTHESIS

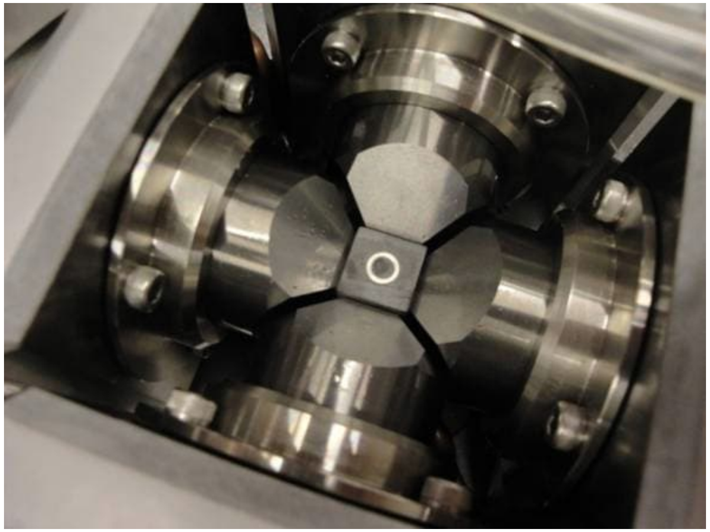
- 5 GPa = 50 000 atm
- 400 – 1200 ^{o}C
- 10 – 120 min
- 50 – 100 mg

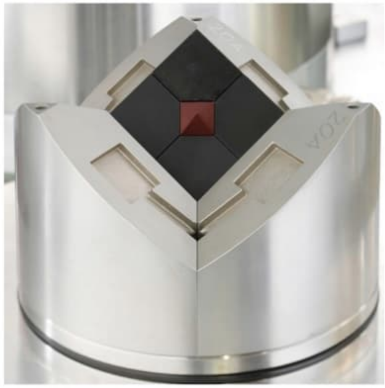
HP equipment
at Tokyo Tech

H. Yamauchi & M. Karppinen, *Supercond. Sci. Technol*. 13, R33 (2000).









HP equipment at Aalto

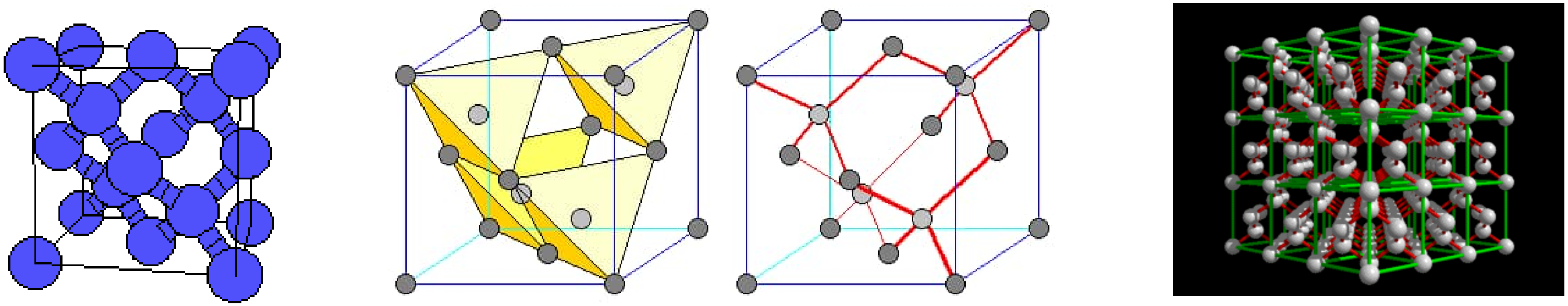
- 4 GPa & 25 GPa

BORON NITRIDE

- Synthesis of boron nitride: $B_2O_3 + NH_3$ at 1000 $^oC \rightarrow$ graphite-type BN
- High-pressure high-temperature treatment → diamond-type BN (so-called boratson)
- Also fullerene-type BN molecules known

DIAMOND STRUCTURE: C and BN

- Each C atom (or B and N atom) bonded with strong covalent bonds to tetrahedrally surrounding neighbours
- In the 3D atom lattice each C-C bond is equally long (1.54 Å) and strong
- All four valence electrons of carbon are bound in the four bonds
  → pure diamond is one of the best known electrical insulators
- Strong covalent bonds → diamond is the strongest material known
- Diamond-type BN is the second strongest material (ca. 50 % of the harness of diamond)
- Strong bonds → high melting point (4100 ^{o}C)



DIAMOND AS THERMAL CONDUCTOR & SEMICONDUCTOR

- Diamond is the best thermal conductor among the known materials

  (ca. 5-times better than the best metals)
- In diamond thermal conduction happens via phonons (vibrations of C atoms)

  [in metals heat (like electricity) transport occurs via moving valence electrons]
- C atoms are light and the C-C bond is strong

  → efficient heat conduction

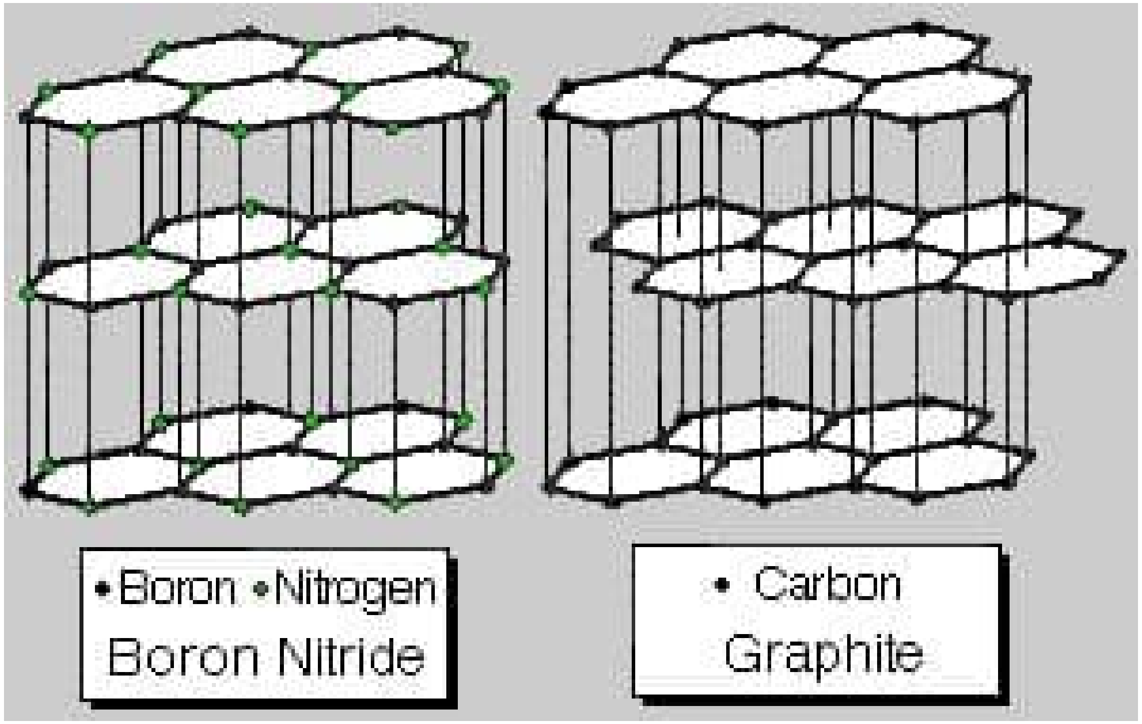
  (impurities and lattice imperfections depress thermal conductivity)
- BN ≈ “impure C”

  → diamond-type BN is not as good thermal conductor as diamond
- Pure diamond is electrical insulator (used as heatsink for semiconductor laser diodes)
- B-doping of diamond → p-type semiconductor
- Diamond-type BN:

  - slight B excess → p-type semiconductor
  - slight N excess → n-type semiconductor

GRAPHITE STRUCTURE: C and BN

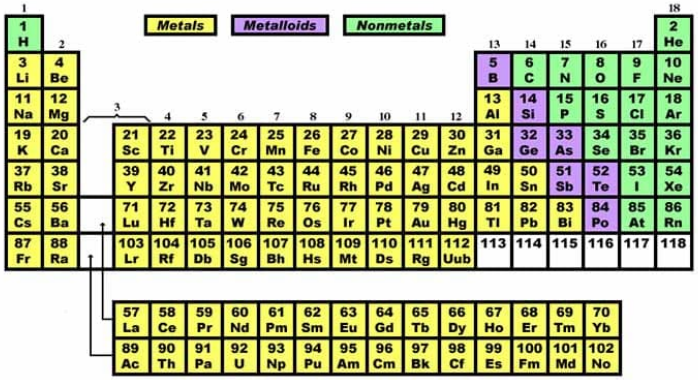
- C: the fourth valence electron loosely bound → good electrical conductivity → black
- BN: Polar bond between the layers → no electrical conductivity → white



METALLIC CHARACTER and BASICITY OF OXIDE: N < P < As < Sb < Bi

- N, P nonmetals, As, Sb semimetals, Bi metal
- However: resistivity increases As < Sb < Bi
- N (*g*), P (*s*; mp. 44 ^{o}C), As (*s*), Sb (*s*), Bi (*s*)
- N_2 gas (:N ≡ N:) but C solid (4 x C-C)
- Melting points (^{o}C):
  N -210, P 44, As subl. 615, Sb 631, Bi 271
  For metals/nonmetals m.p. decreases/increases in a group from up to down
- Oxidation states: N: -III ... +V
  P: -III, +III, +IV, +V
  As, Sb, Bi: +III, +V (Bi: inert-pair effect)
- Acid-base nature of oxide reflects the (non)metal character of the element

  - N oxides (+I ... +V), P_2O_3 and P_2O_5 acidic
  - As_2O_3, As_2O_5 and Sb_2O_3 amfoteric
  - Bi_2O_3 basic

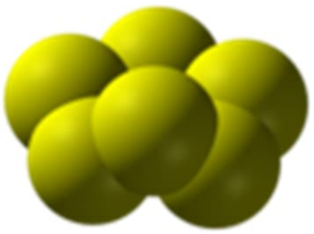


Metals | Metalloids | Nonmetals

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113	114	115	116	117	118
		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

MULTITUDE OF SULPHUR COMPOUNDS

- **Several stable oxidation states**
- **Allotropy of S: tens of allotropes (ref. O 2, Se 6, Te 3, Po 2)**
- **Various S-chains and S-rings, where other atoms can bond**
- **Most common: S_8-ring ”crowne” (different polymorfs)**
- **Polycations S_n^{2+} ($n=4$ yellow, $n=8$ blue, $n=19$ red)**
- **Polysulfides S_n^{2-} ($n=2-6$; strongly colourful)**
- **Thio-compounds**
- **Sulphur is also one of the basic elements in organic compounds**



HALOGENS

Chemically very homogeneous group, except fluorine which differs from the rest of the group members in many ways

Element	Melting Point (°C)	Boiling Point (°C)
F_2	-219	-188
Cl_2	-101	-34
Br_2	-7	+60
I_2	+114	+185
As .(rad. act)	+320	+337

FLUORINE *VERSUS* OTHER HALOGENS

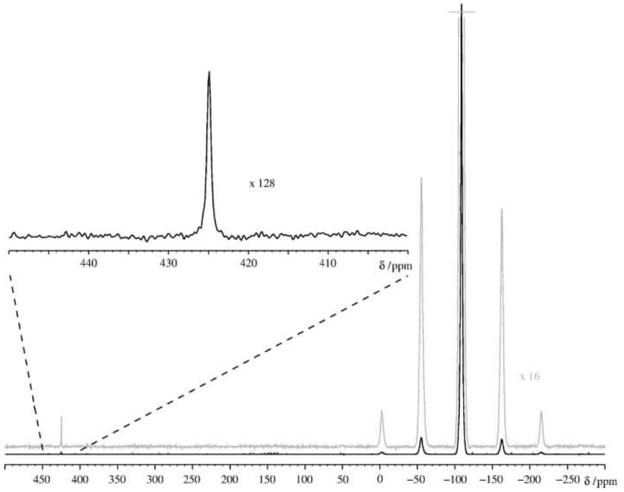
- **Atomic radius (Å): F 0.71, Cl 0.99, Br 1.14, I 1.33**
- **Electronegativity: F 4.0, Cl 3.0, Br 2.8, I 2.5, At 2.2**
- **Dissosiation energy (kJ/mol): F 155, Cl 240, Br 190, I 149, At 116**
- **Oxidation states:**
  F: -I
  Cl: -I, +I, (+II), +III, (+IV), +V, (+VI), +VIII
  Br: -I, +I, +III, (+IV), +V, (+VI), +VIII
  I: -I, +I, +III, +V, +VIII

Small F atoms
→ Large electron-electron repulsion in F_2
→ Small bond energy
→ Highly reactive

Preparation of fluorine (from fuorite CaF_2) Moissan 1886 (Nobel 1906):
- $2HF \rightarrow H_2 + F_2$
- problem: F_2 and HF gases highly reactive and poisonous
- electrolysis in KF melt, Pt cell, Pt-Ir electrodes, -50 °C

Antozonite (Stink Spar)

- The CaF_2 mineral “Stink Spar” in Wölsendorf contains minute amounts of radioactive uranium inclusions
- Uranium constantly emits ionizing radiation which splits CaF_2 into calcium and elemental fluorine
- The thus formed fluorine remains in tiny inclusions
- It however slowly reacts with atmospheric oxygen and water vapour, producing ozone
- The characteristic smell of ozone gave the name for the mineral



2012: First proof of F_2 on Earth by ^{19}F-MAS-NMR

J. Schmedt auf der Günne, M. Mangstl & **F. Kraus**, *Angew. Chem. Int. Ed.* **51**, 7847 (2012).

- Fluorine obeys always the octet rule

  (only one covalent bond possible)

- Large electronegativity

  → strong oxidizer

  → promotes high oxidation states for cations *

  → compounds ionic

  → strong hydrogen bonds

* Cations often have higher oxidation states in oxides compared to fluorides,
e.g. OsO_4 possible, but not OsF_8
Reason: 8 F^- ions around Os^{8+} cation not possible !

NOBLE GASES: BASIC PROPERTIES

- **Helium has the lowest known boiling point (-269 ^{o}C)**
- **Ionization energies (kJ/mol):**
  He 2269, Ne 2079, Ar 1519, Kr 1349, Xe 1169, Rn 1036

COMPOUNDS

- **Bartlett 1962: $O_2(g) + PtF_6(g) \rightarrow [O_2^+][PtF_6^-](s)$**
- **Ionization energy of O_2 1180 kJ/mol $\approx$ IE(Xe)**
  → "$[Xe][PtF_6]$" → Ar, Kr, Xe form compounds with the most electronegative elements
- **Oxidation states: +II, +IV, +VI, +VIII**
- **Bond strengths (kJ/mol): Xe-F 130, Xe-O 84, Kr-F 50**
- **$KMXeNaO_6$ double perovskite !**
  [S.N. Britvin et al., Angew. Chem. 127, 1 (2015)]

SUPERFLUIDS

- Under normal pressure He stays in liquid state down to 0 K
- ^{3}He and ^{4}He superfluids at low temperatures
- Viscosity zero → continuous movement → escape from the container
- Laws of classical mechanics do not work → quantum mechanics
- Ultrahigh thermal conductivity