

LECTURE SCHEDULE

	Date	Topic
1.	Wed 28.10.	Course Introduction & Short Review of the Elements
2.	Fri 30.10.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri 06.11.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Wed 11.11.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
5.	Fri 13.11.	Redox Chemistry
6.	Mon 16.11.	Transition Metals: General Aspects & Crystal Field Theory
7.	Wed 18.11.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
8.	Fri 20.11.	V, Nb, Ta & Metal Complexes and MOFs
9.	Mon 23.11.	Cr, Mo, W & 2D materials
10	Wed 25.11.	Mn, Fe, Co, Ni, Cu & Magnetism and Superconductivity
11.	Fri 27.11.	Resources of Elements & Rare/Critical Elements & Element Substitutions
12.	Mon 30.11.	Lanthanoids + Actinoids & Pigments & Luminescence & Upconversion
13.	Wed 02.12.	Inorganic Materials Chemistry Research

EXAM: Thu Dec 10, 9:00-12:00 Ke1

PRESENTATION TOPICS/SCHEDULE

Wed 18.11. Ti: Ahonen & Ivanoff

Mon 23.11. Mo: Kittilä & Kattelus

Wed 25.11. Mn: Wang & Tran
Ru: Mäki & Juopperi

Fri 27.11. In: Suortti & Räsänen
Te: Kuusivaara & Nasim

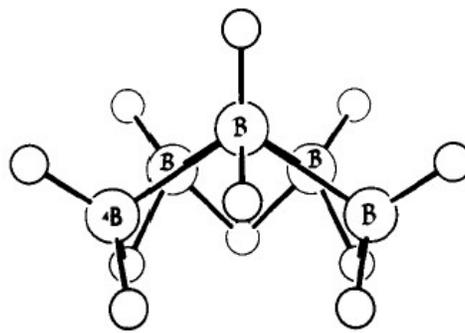
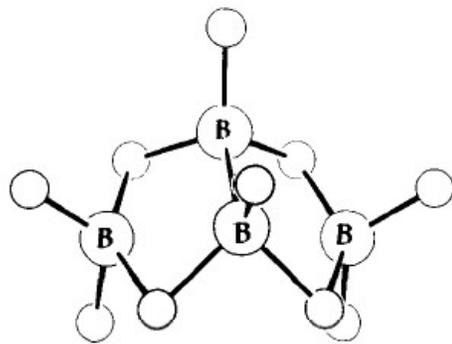
Mon 30.11. U: Musikka & Seppänen

QUESTIONS: Lecture 3

Name your file Exe-3-Familyname; Return by 4 pm into MyCourses drop-box

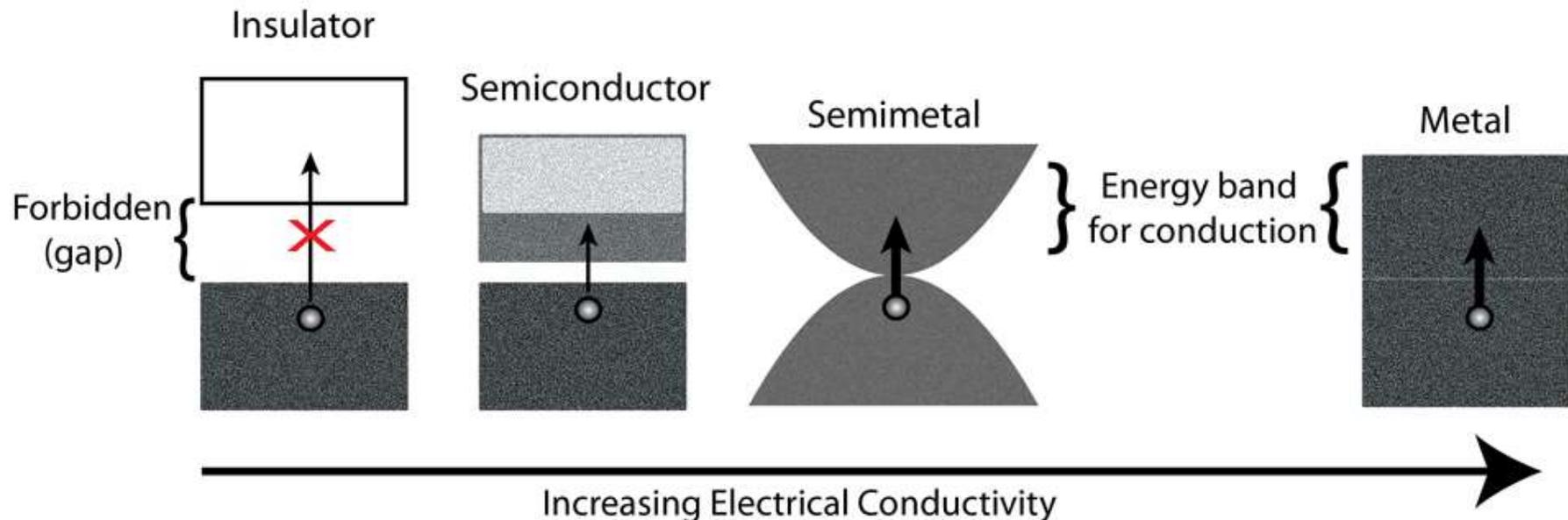
1. Name four main group elements which you consider to be most unique; also give the most characteristic property for each of these elements.

2. Draw semitopological diagrams for the following boranes: B_4H_{10} and B_5H_{11}



Metalloids

- Elements with properties intermediate between those of typical metals and nonmetals: boron, silicon, germanium, arsenic, antimony, tellurium & polonium
- Around 1950s: *metalloid* (originally: metalloid = nonmetal)
- Sometimes: metalloid \approx 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)



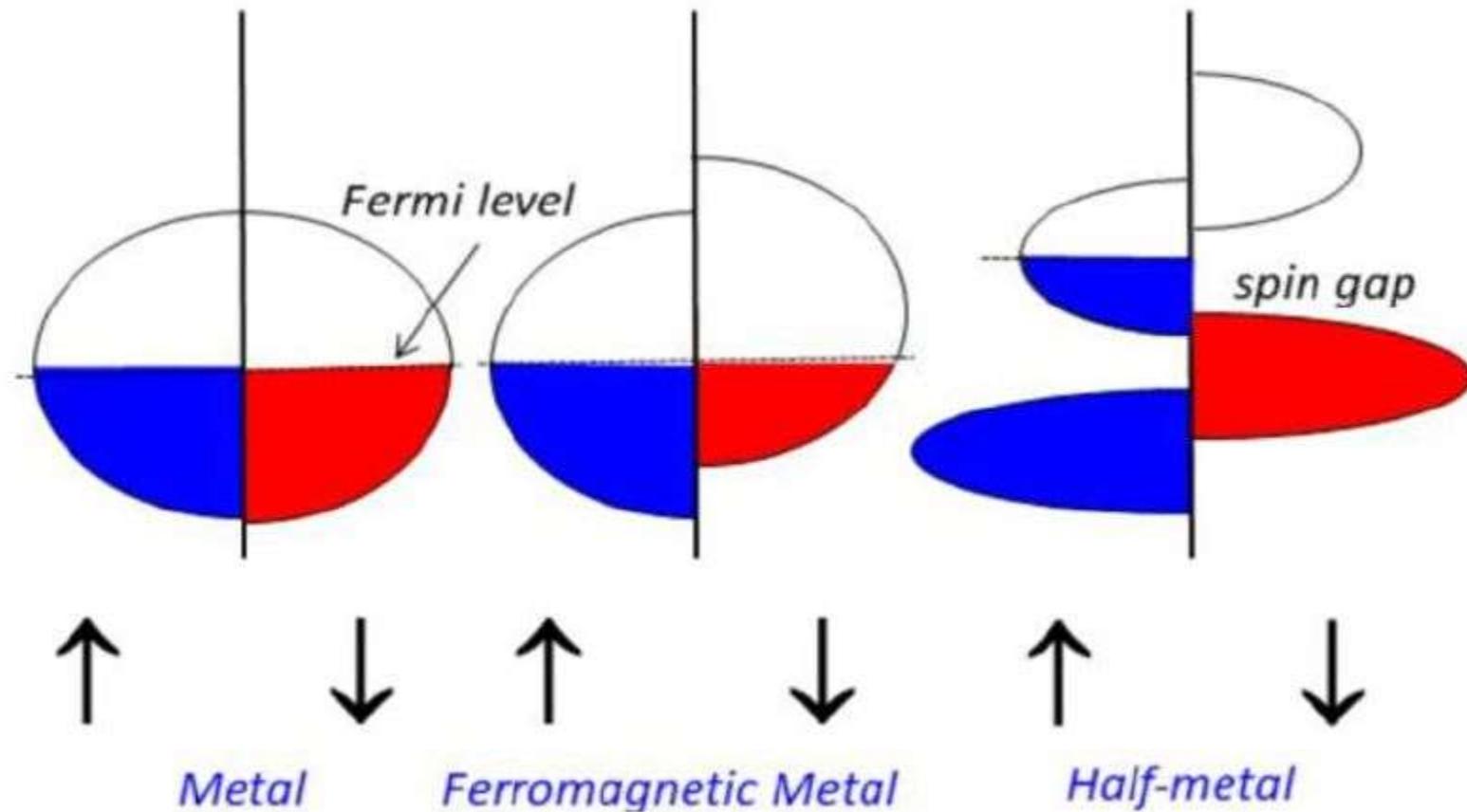
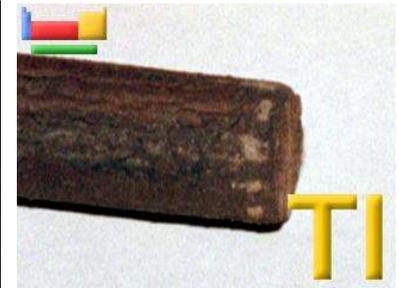
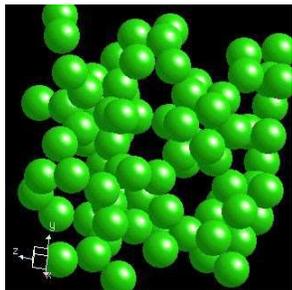


Fig. 1. Band structure diagrams for a metal, ferromagnetic metal and a half-metal



BORON GROUP: MELTING POINTS

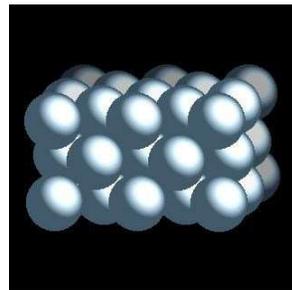
2180 °C



Boron

Rhombohedral

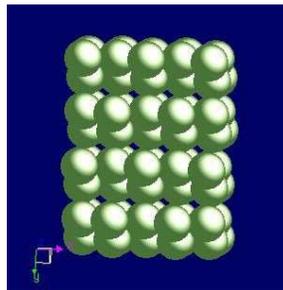
660 °C



Aluminum

CCP

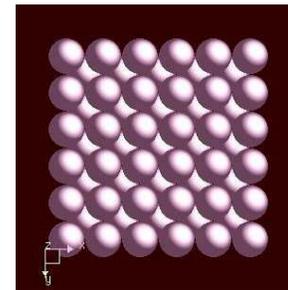
30 °C



Gallium

Orthorhombic

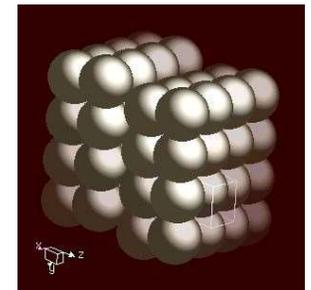
157 °C



Indium

Tetragonal

303 °C



Thallium

HCP

BORON: ELECTRON DEFICIENT COMPOUNDS

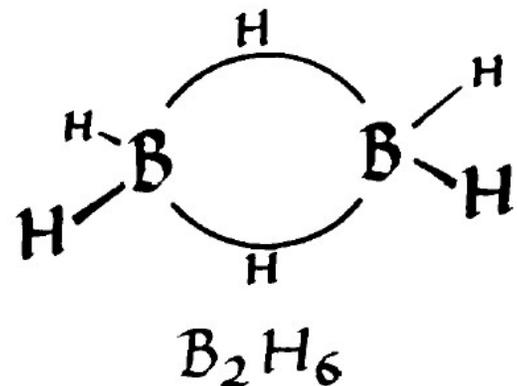
- B: $1s^2 2s^2 2p^1$
3 valence electrons → octet not possible with covalent bonds
electronegativity 2.0 → ionic bonds not possible
- Difficult to achieve electron octet → *electron deficient* compounds
- Hydrogen compounds of boron, **boranes**, are typical examples of electron deficient compounds
- Also Al, Ga, Be and Li form electron deficient compounds:
 $(\text{AlH}_3)_n$, $\text{Al}_2(\text{CH}_3)_6$, $[\text{Be}(\text{CH}_3)_2]_n$, $[\text{Li}(\text{CH}_3)]_4$
- Normal single bond: 2 atoms and 2 bond electrons (2c-2e)
- Electron deficient compound: 3 atoms and 2 bond electrons (3c-2e)

BORANES

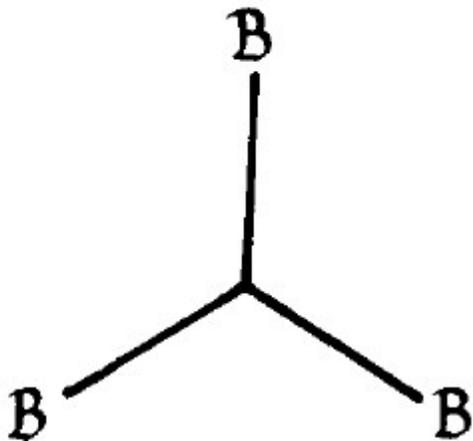
- B_nH_{n+4} or B_nH_{n+6} ($n = 2-20$)
- First synthesized by Alfred Stock 1909:
 $MgB_2 + HCl \rightarrow B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_{10}H_{14}, \dots$
- Air-sensitive compounds
→ closed system, inert synthesis atmosphere
- Naming:
number of B atoms with prefix,
number of H atoms in 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

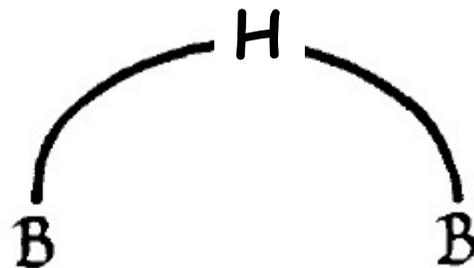
- William Lipscomb (Nobel 1976)
- Bonds: B-H (terminal 2c-2e)
 B-H-B (3c-2e)
 B-B (2c-2e)
 B-B-B (3c-2e)



2-center



3-center central



3-center open

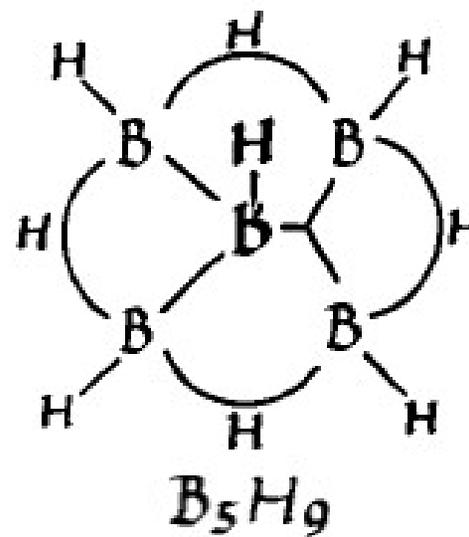
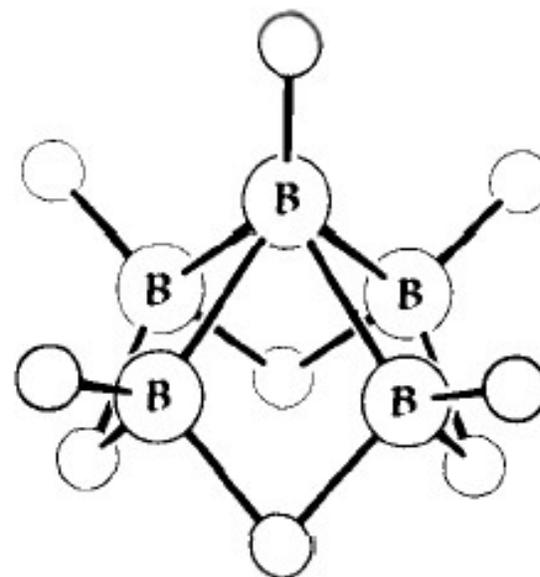
EXAMPLE: B_5H_9

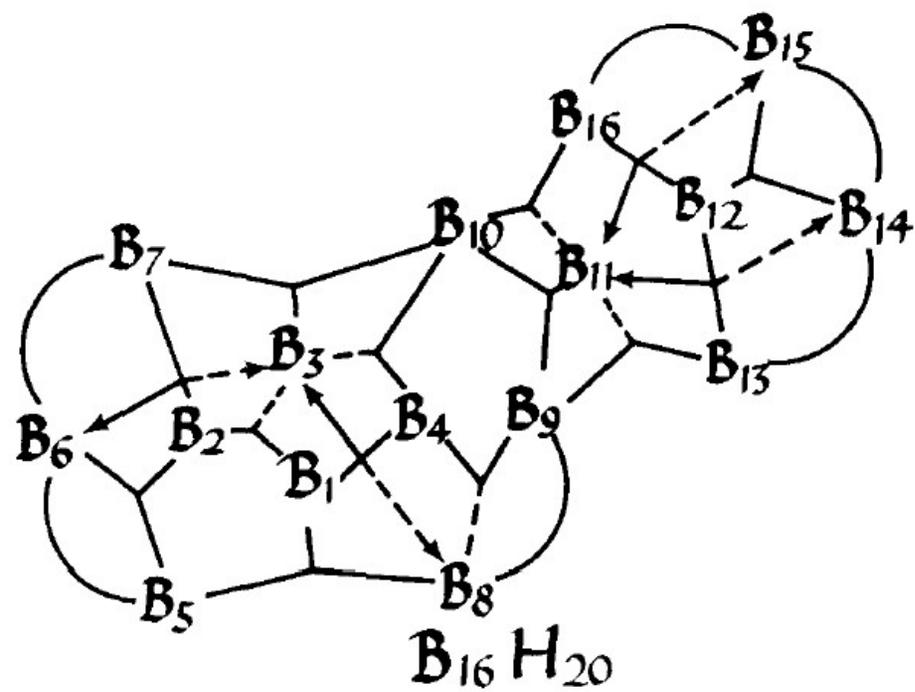
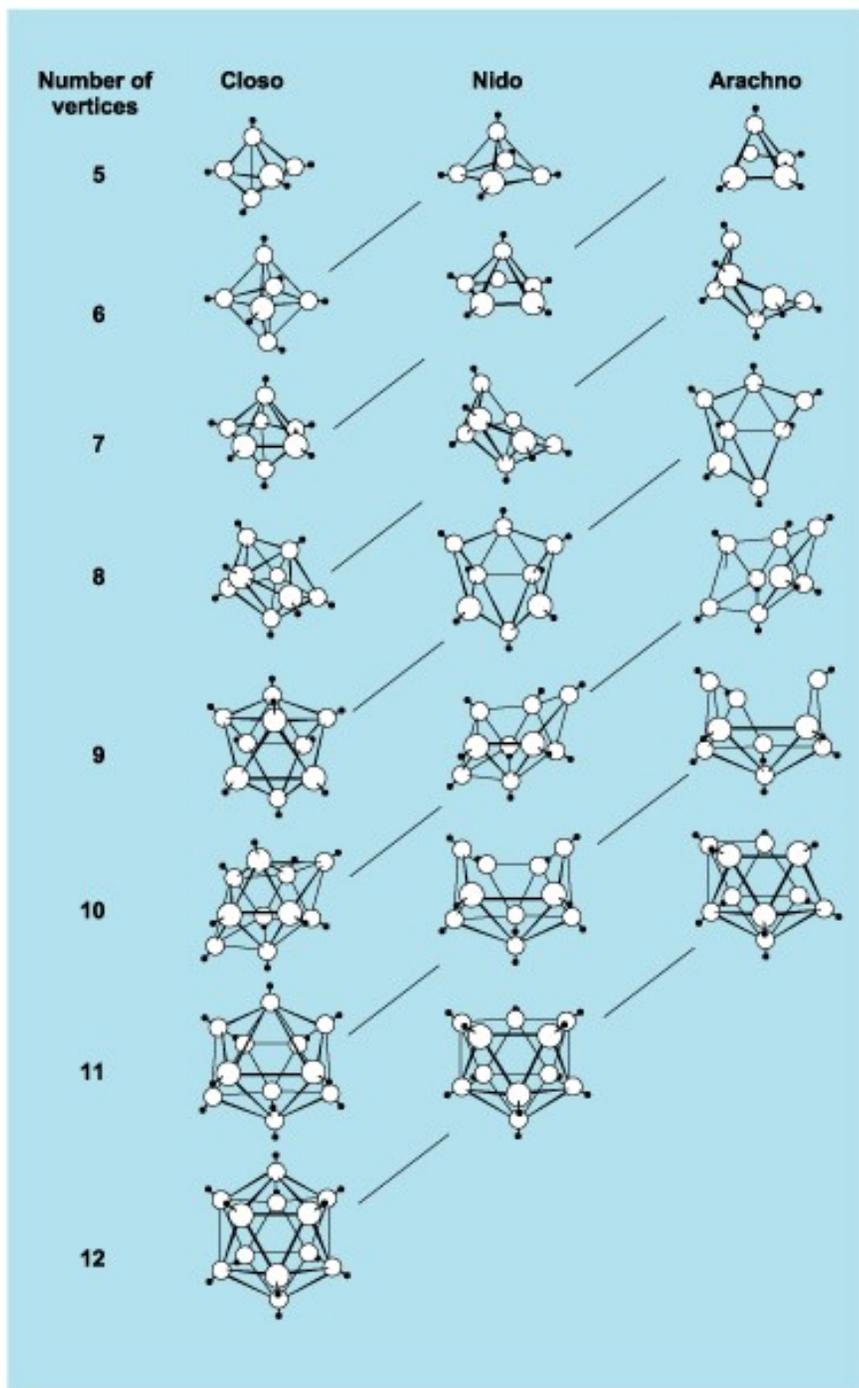
Valence electrons:

$$5 \times 3e + 9 e = 24 e$$

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





BORIDES

■ Binary compounds of boron with metals

- more than 200 different compounds
- stoichiometry varies $M_5B \dots MB_{66}$
(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: $^1_0n + ^{10}_5B \rightarrow ^7_3Li + ^4_2He$)



■ Boron carbide

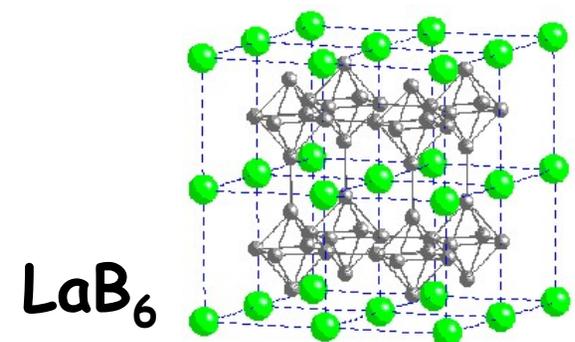
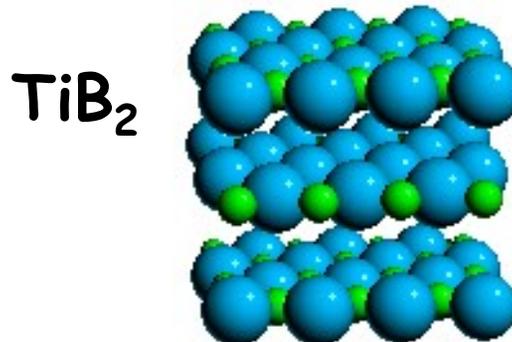
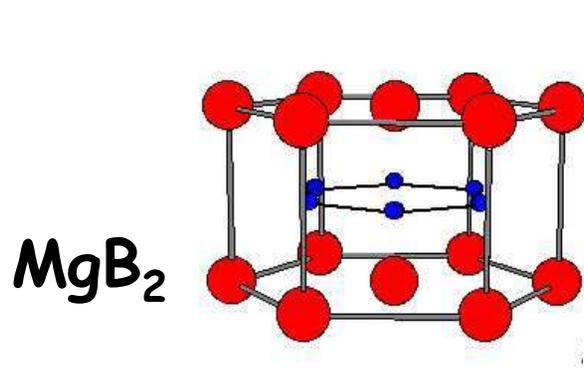
- “ B_4C ” = $B_{12}C_3$
- one of the hardest materials
- uses: armor material, bicycles



BORIDE STRUCTURES

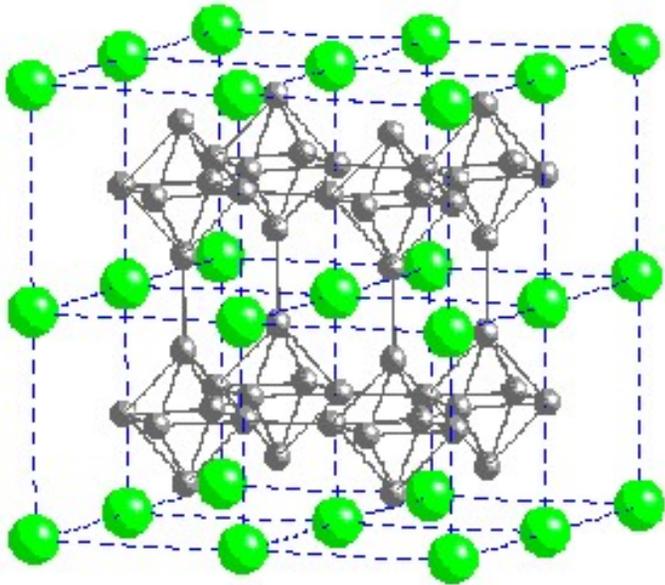
- **M-rich:**
 - (1) separate B atoms
 - (2) separate B₂ atom pairs
 - (3) B_n chains
 - (4) double chains
 - (5) planes (MB₂)

(catenation tendency of B atoms increases with increasing B content)
- **B-rich:**
 - (1) planes
 - (2) 3D nets
 - (3) clusters (e.g. B₆ octahedra and B₁₂ icosahedra)



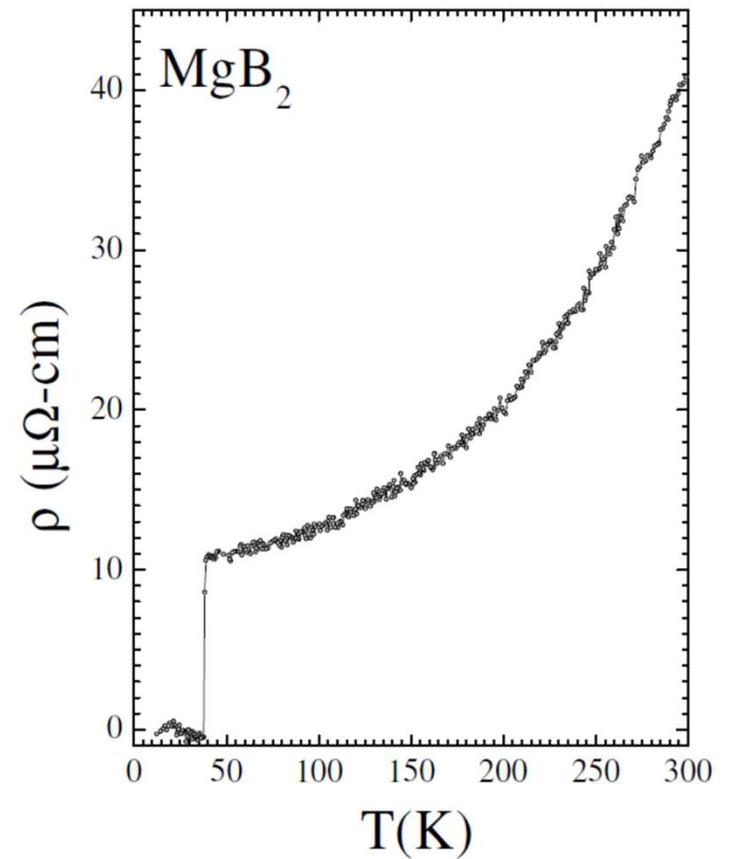
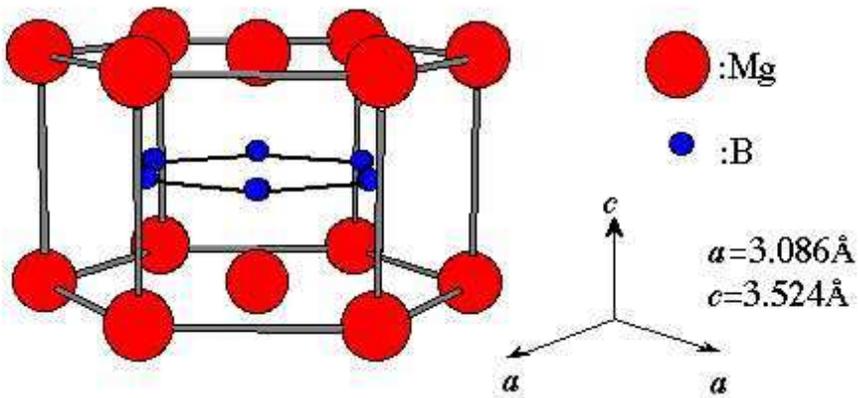
BONDING in BORIDES

- The simple ionic / covalent / metal bond concepts fail
- **LaB₆**:
 - in B₆ clusters electron-deficient (multicenter-2e) bonds
 - between clusters covalent (2c-2e) B-B bonds
 - move of two electrons from **La** to B₆ cluster
 - La²⁺-B₆²⁻ 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 $(\text{B}_{12}\text{H}_{11}\text{SH})^{2-}$ ion based ones have a tendency to accumulate in cancer cells



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} cm²

Graphene

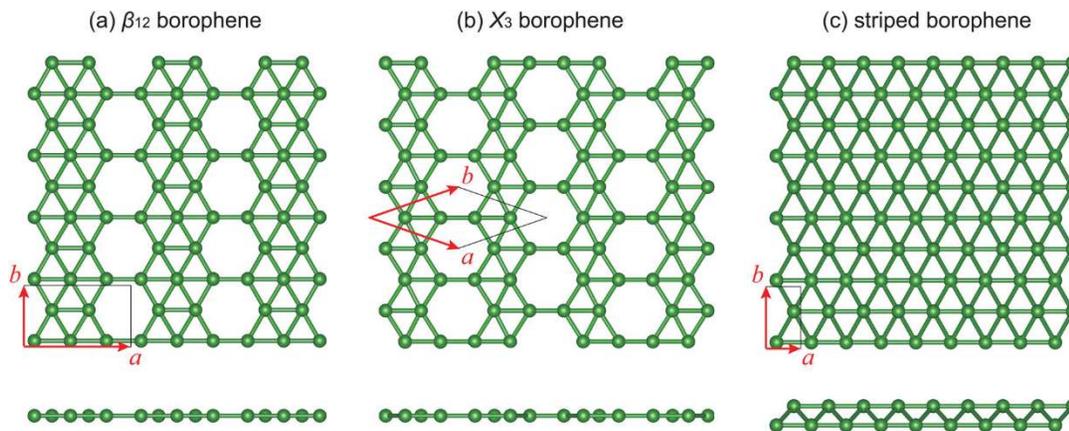
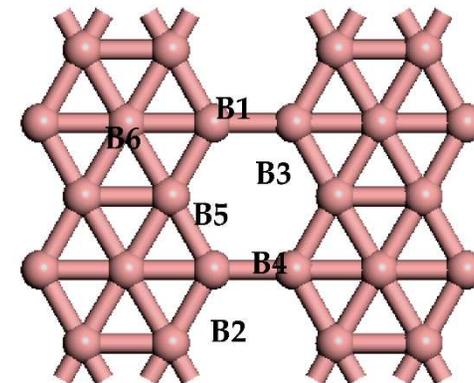
Geim & Novoselov (Univ. Manchester)
2004; Nobel (physics) 2010



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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



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

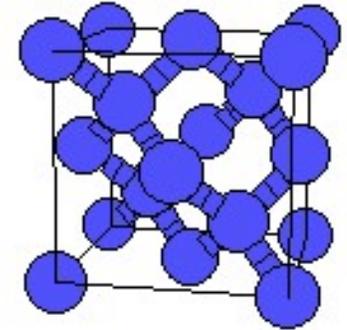
A.J. Mannix, et al., Synthesis of borophenes: anisotropic, two-dimensional boron polymorphs, *Science* 350, 1513 (2015).

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

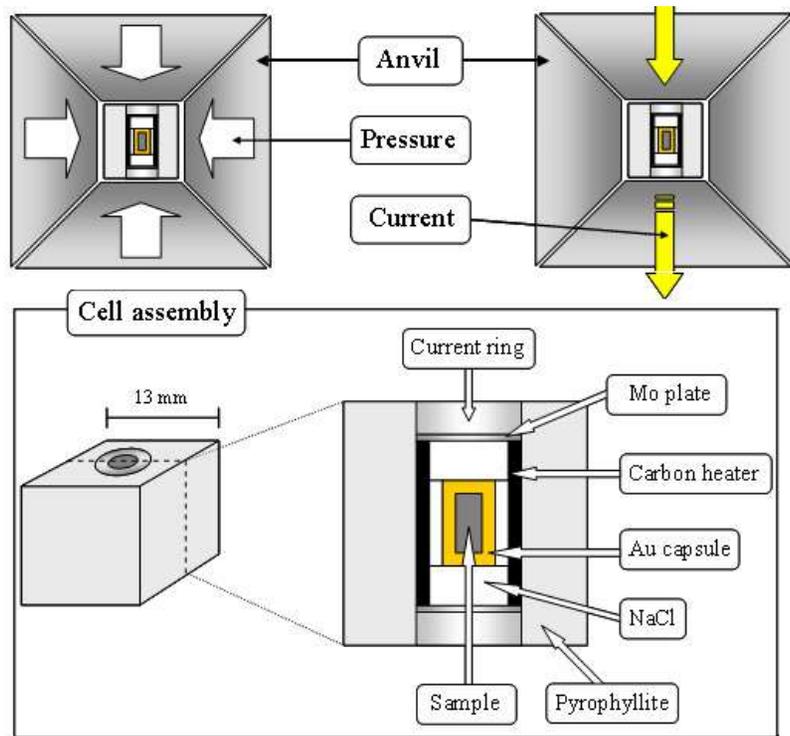
ISOELECTRONIC: C-C and B-N

- Catenation (= chain-formation capability) typical for the carbon group (ref. organic chemistry)
- Catenation capability decreases: $C > Si > Ge > Sn > Pb$ (after C the next in catenation capability is S)
- Also in the elemental form the C-C bond is strong, ref. carbon allotropes: graphite, **diamond**, fullerenes, nanotubes and graphene
- 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

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 combustion experiments were made in the end of 18th century: diamond and graphite produce the same amount of CO₂ (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/cm³) compared to the graphite (2.3 g/cm³); 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)

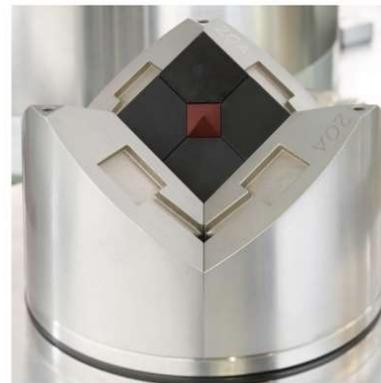
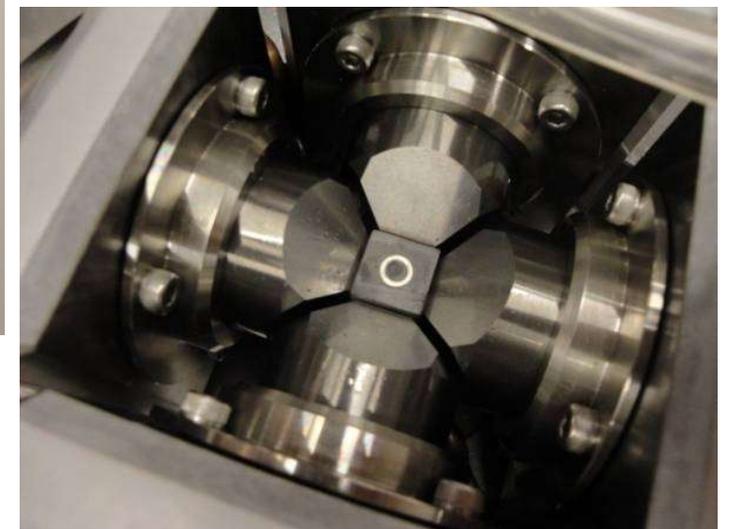
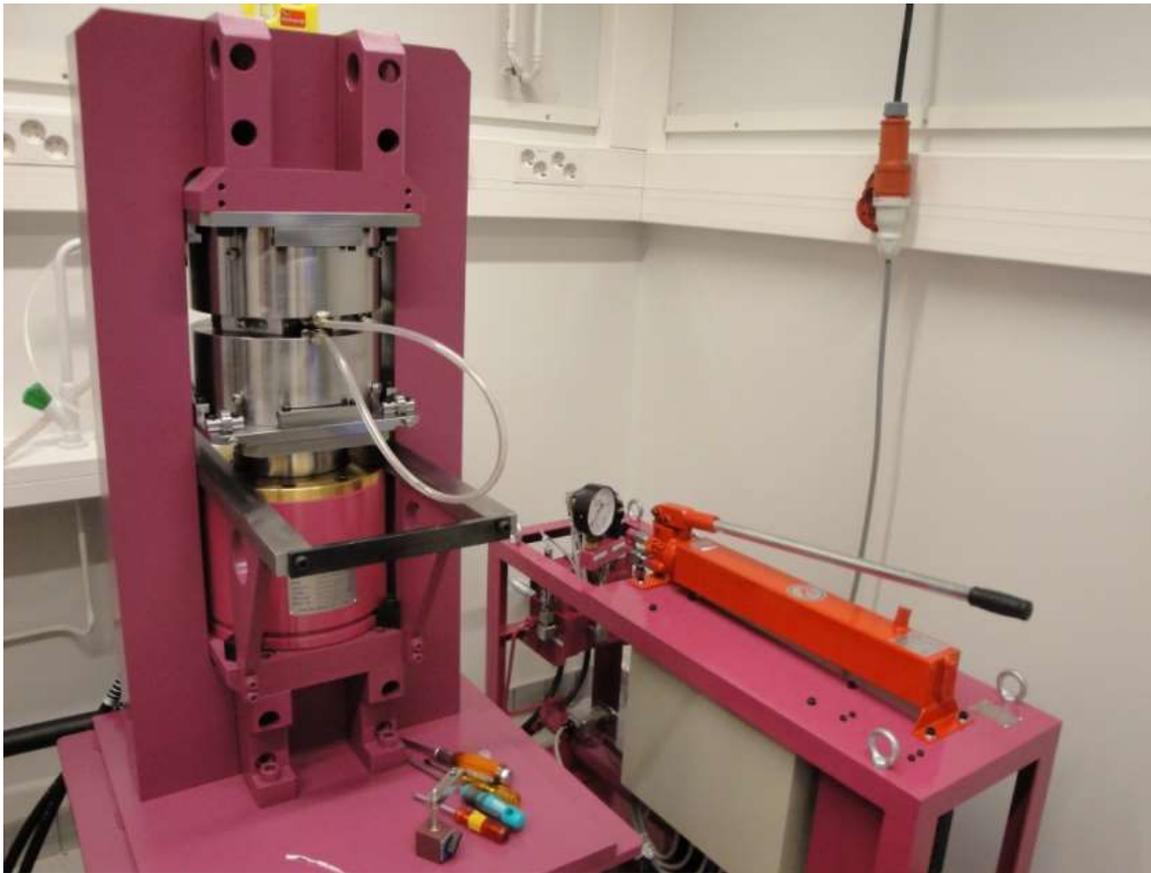


HIGH-PRESSURE SYNTHESIS

- 5 GPa = 50 000 atm
- 400 – 1200 °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

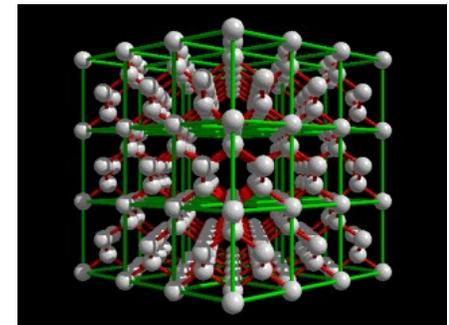
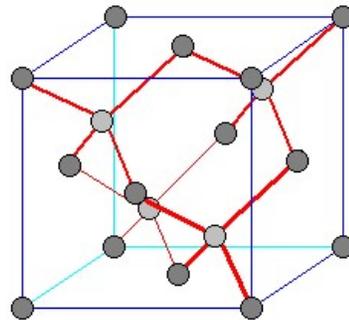
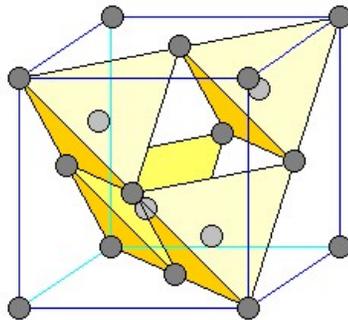
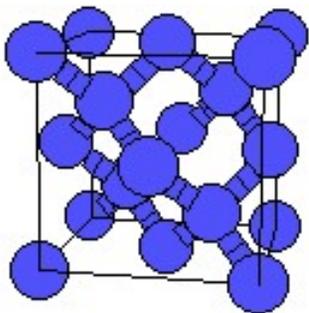
- 4 GPa & 25 GPa

BORON NITRIDE

- Synthesis of boron nitride: $B_2O_3 + NH_3$ at 1000 °C → 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 °C)

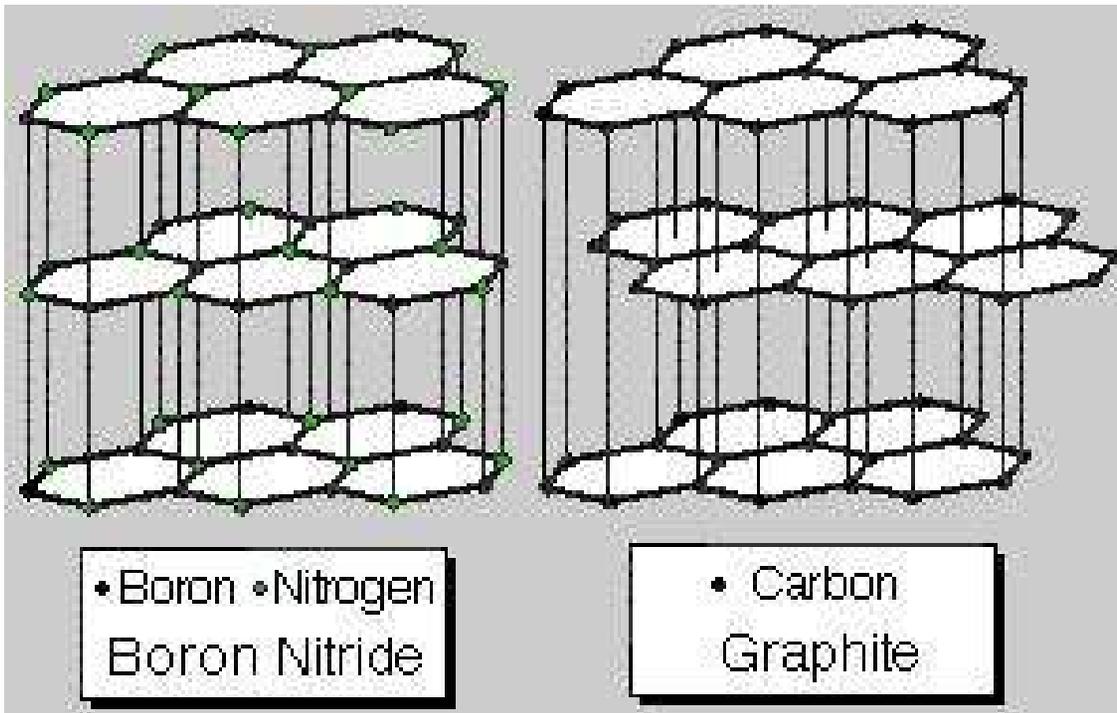


DIAMOND AS THERMAL CONDUCTOR & SEMICONDUCTOR

- 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 \approx “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 °C), As (s), Sb (s), Bi (s)
- N₂ gas (:N ≡ N:) but C solid (4 x C-C)
- Melting points (°C):
N -210, P 44, As subl. 615, Sb 631, Bi 271

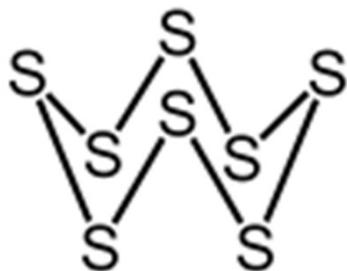
Metals										Metalloids			Nonmetals					
1 H	2												13 B	14 C	15 N	16 O	17 F	18 Ne
3 Li	4 Be											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
11 Na	12 Mg	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
19 K	20 Ca	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
37 Rb	38 Sr	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	
55 Cs	56 Ba	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	
87 Fr	88 Ra																	
		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			

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), P₂O₃ and P₂O₅ acidic
 - As₂O₃, As₂O₅ and Sb₂O₃ amfoteric
 - Bi₂O₃ basic

MULTITUDE OF SULPHUR COMPOUNDS

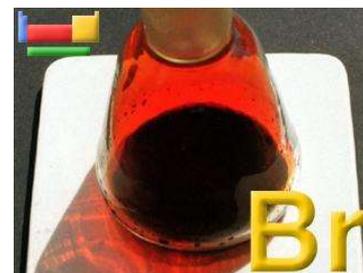
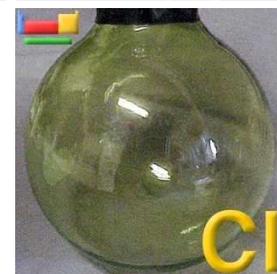
- Several stable oxidation states
- Allotropy of S: tens of allotropes (ref. O 2, Se 6, Te 3, Po 2)
- Various S-chains and S-rings, where other atoms can bond
- Most common: S₈-ring "crown" (different polymorfs)
- Polycations S_n²⁺ (*n*=4 yellow, *n*=8 blue, *n*=19 red)
- Polysulfides S_n²⁻ (*n*=2-6; 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
- Dissociation 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 F₂
- Small bond energy
- Highly reactive

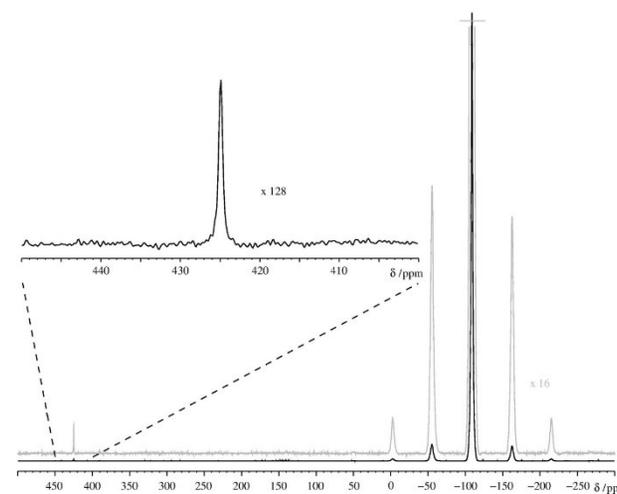
Preparation of fluorine (from fluorite CaF₂) Moissan 1886 (Nobel 1906):

- $2\text{HF} \rightarrow \text{H}_2 + \text{F}_2$
- problem: F₂ 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 °C)
- Ionization energies (kJ/mol):
He 2269, Ne 2079, Ar 1519, Kr 1349, Xe 1169, Rn 1036

COMPOUNDS

- Bartlett 1962: $\text{O}_2(g) + \text{PtF}_6(g) \rightarrow [\text{O}_2^+][\text{PtF}_6^-](s)$
- Ionization energy of O_2 1180 kJ/mol \approx IE(Xe)
→ “[Xe][PtF₆]” → 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
- ^3He and ^4He superfluids at low temperatures
- Viscosity zero \rightarrow continuous movement \rightarrow escape from the container
- Laws of classical mechanics do not work \rightarrow quantum mechanics
- Ultrahigh thermal conductivity

