TENTATIVE LECTURE SCHEDULE

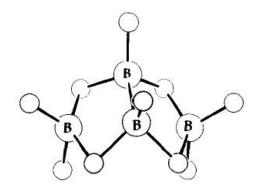
		Date	Торіс
1.	Mon	13.09.	Course Introduction & Short Review of the Elements
2.	Wed	15.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	17.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Mon	20.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Wed	22.09.	Transition Metals: General Aspects & Pigments
6.	Mon	27.09.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
7.	Wed	29.09.	Redox Chemistry
8.	Mon	04.10.	Crystal Field Theory
9.	Wed	06.10.	V, Nb, Ta & Metal Complexes & MOFs
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
12.	Wed	13.10.	EXTRA
13.	Fri	15.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Mon	18.10.	Lanthanoids + Actinoids & Luminescence (Down/Upconversion)
15.	Wed	20.10.	Inorganic Materials Chemistry Research

EXAM: Thu Oct. 28, 2021

QUESTIONS: Lecture 3

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

- The following main group elements may be considered quite unique among all the elements, regarding one or more chemical or physical feature: B, F, He. Explain which feature(s)?
- 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}

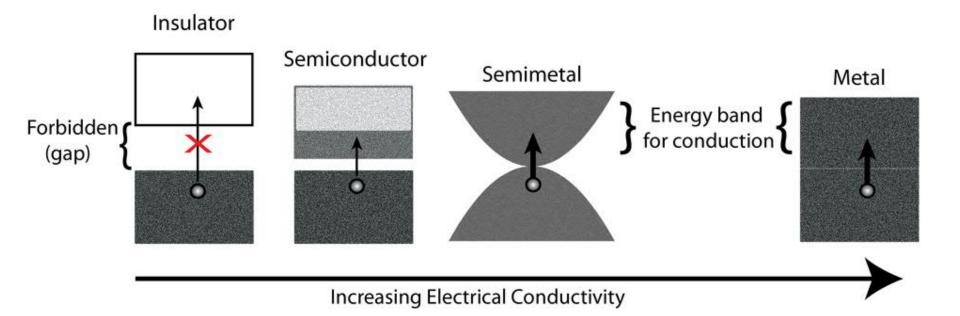


1 1 H	2			Met	als	M	etallo	ids	N	lonme	tals	1	13	14	15	16	17	18 2 He
3 Li	4 Be	1											5 B	6 C	7 N	8	9 F	10 Ne
11 Na	12 Mg	_	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 CI	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 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 1	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 TI	82 Pb	83 Bi	84 Po	85 At	86 Rr
87 Fr	88 Ra	Ť	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	11
Fr	1000	Ţ		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	and the second second	Sg				1000		10000	113	114	115	110		Ľ
			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	90	91	92 U	93 Np	94 Pu	95	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

TODAY

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 ≈ 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)



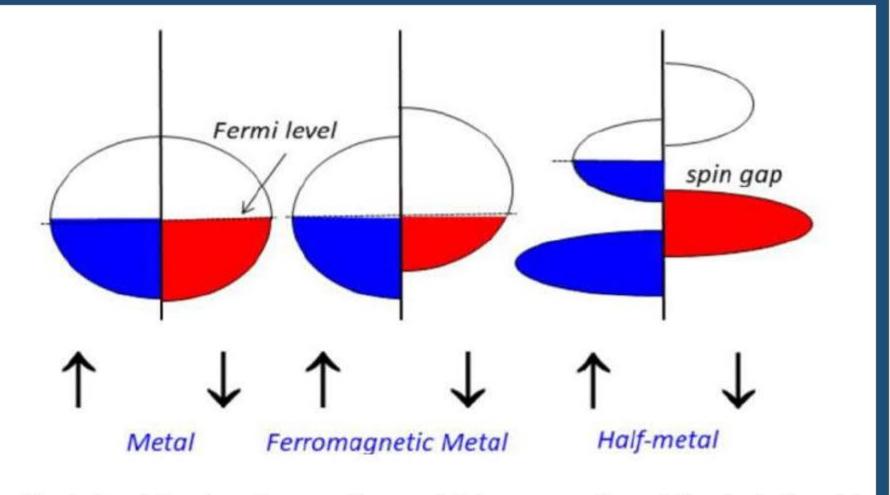


Fig. 1. Band structure diagrams for a metal, ferromagnetic metal and a half-metal

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: $E-O-H \rightarrow E^+ + OH^-$ (base)
- large electronegativity: $E-O-H \rightarrow E-O^{-} + H^{+}$ (acid)
- For example: elements of the third period:

NaOHstrong base $Mg(OH)_2$ base $AI(OH)_3$ amfolyte $Si(OH)_4$ weak acid $[H_4SiO_4]$ $OP(OH)_3$ acid $[H_3PO_4]$ $O_2S(OH)_2$ strong acid $[H_2SO_4]$ $O_3CI(OH)$ strong acid $[HCIO_4]$

Electronegativity increases



BORON GROUP: MELTING POINTS

2180 °C	660 °C	30 °C	157 °C	303 °C
Boron	Aluminum	Gallium	Indium	Thallium
Rhombohedral	ССР	Orthorhombic	Tetragonal	НСР

BORON: ELECTRON DEFICIENT COMPOUNDS

■ B: 1*s*²2*s*²2*p*¹

3 valence electrons \rightarrow octet not possible with covalent bonds electronegativity 2.0 \rightarrow ionic bonds not possible

- Difficult to achieve electron octet \rightarrow electron deficient compounds
- Hydrogen compounds of boron, boranes, are typical examples of electron deficient compounds
- Also AI, Ga, Be and Li form electron deficient compounds: (AIH₃)_n, Al₂(CH₃)₆, [Be(CH₃)₂]_n, [Li(CH₃)]₄
- Normal single bond: 2 atoms and 2 bond electrons (2c-2e)
- Electron deficient compound: 3 atoms and 2 bond electrons (3c-2e)

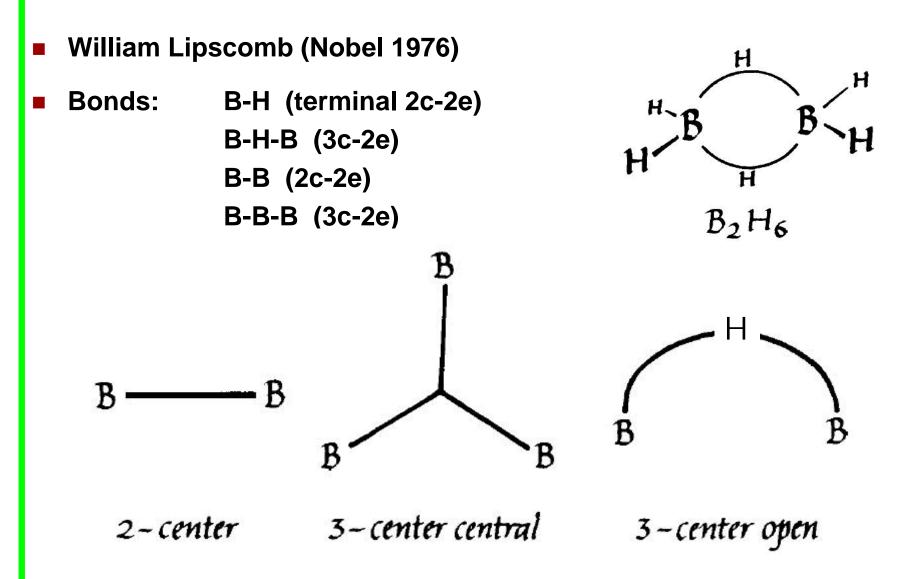
BORANES

- $B_n H_{n+4}$ or $B_n H_{n+6}$ (*n* = 2-20)
- First synthesized by Alfred Stock 1909: $MgB_2 + HCI \rightarrow B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_{10}H_{14}, ...$
- Air-sensitive compounds
 - \rightarrow 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



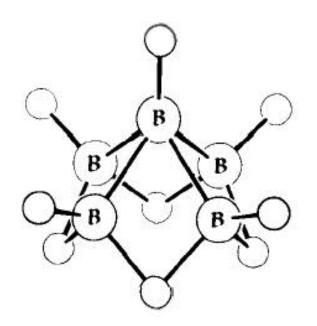
EXAMPLE: B_5H_9

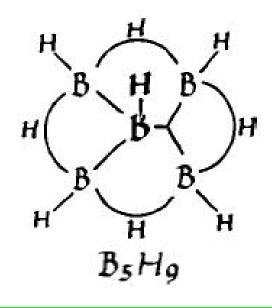
Valence electrons:

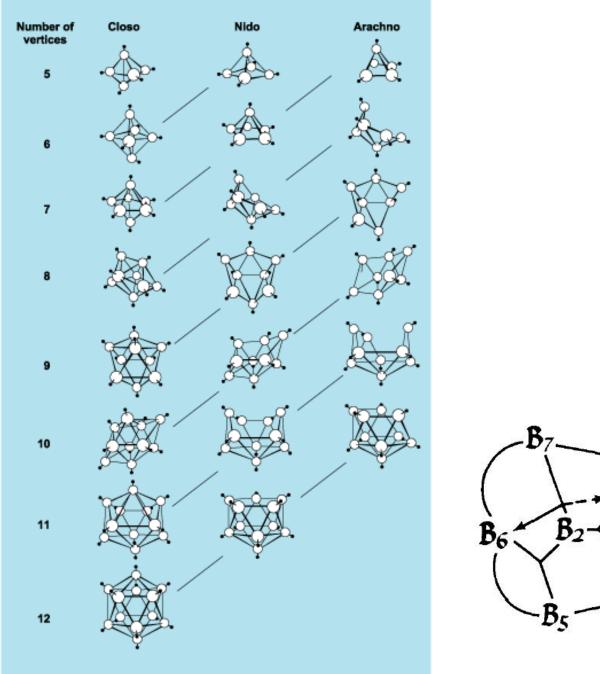
5 x 3e + 9 e = 24 e

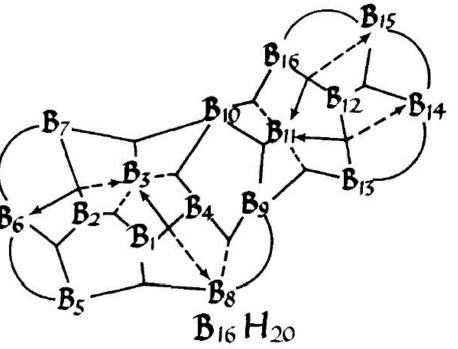
Bonds:

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









BORIDES

- Binary compounds of boron with metals
 - more than 200 different compounds
 - stoichiometry varies M₅B ... MB₆₆
 (e.g. M₂B, MB, MB₂, MB₄, MB₆)
 - 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: ${}^{1}n + {}^{10}B \rightarrow {}^{7}Li + {}^{4}He$)
- Boron carbide
 - " B_4C " = $B_{12}C_3$
 - one of the hardest materials
 - uses: armor material, bycycles



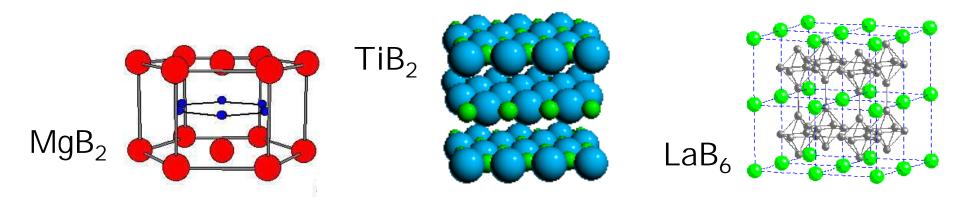


BORIDE STRUCTURES

- M-rich: (1) separate B atoms
 - (2) separate B_2 atom pairs
 - (3) B_n chains
 - (4) double chains
 - (5) planes (MB₂)

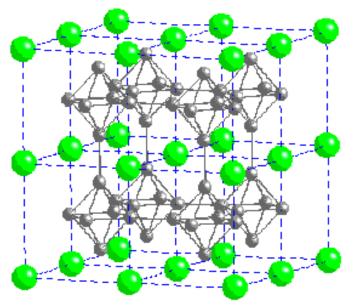
(catenation tendency of B atoms increases with increasing B content)

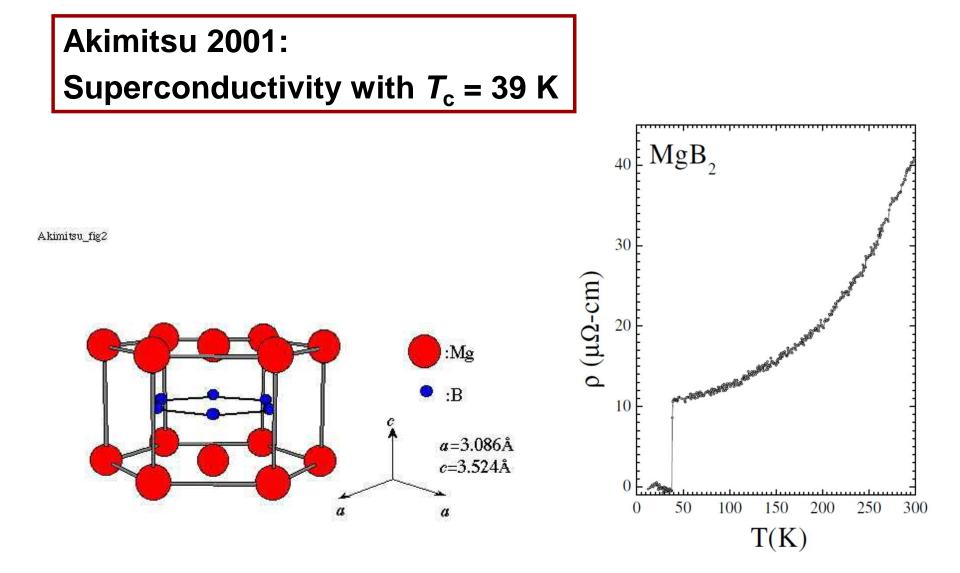
- B-rich:
- (1) planes
- (2) 3D nets
- (3) clusters (e.g. B₆ octahedra and B₁₂ icosahedra)



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
 - \rightarrow La²⁺-B₆²⁻ ionic bond
 - third valence electron of La is delocalized (metal bond)
 - \rightarrow good electrical conductivity, good electron emission
 - \rightarrow use: electron guns in electron microscopes





BORON-NEUTRON-CAPTURE-THERAPY (BNCT)

- Treatment of inoperable brain tumors/cancer
- Boron (¹⁰B) absorbs efficiently neutrons (large absorption cross section)
 → radioactive ¹¹B:a
- Radioactive radiation destroys tumor cells
- Challenge: to deliver high concentrations of a boron compound specifically to tumor cells
- Some boron compounds such as (B₁₂H₁₁SH)²⁻ ion based ones have a tendency to accumulate in cancer cells

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

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

 $1 \text{ barn} = 10^{-24} \text{ cm}^2$

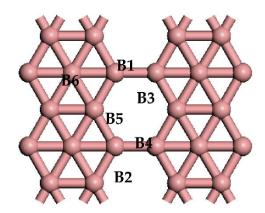
Graphene

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

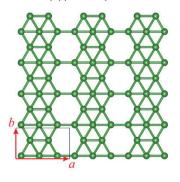


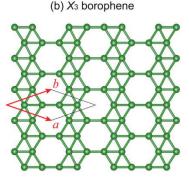
I. Boustani, New quasi-planar surfaces of bare boron, Surface Science 370, 355 (1997).

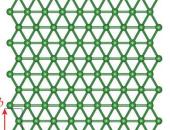
A.J. Mannix, et al., Synthesis of borophenes: anisotropic, twodimensional boron polymorphs, Science 350, 1513 (2015).

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









(c) striped borophene

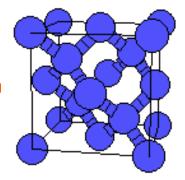


ISOELECTRONIC: C-C and B-N

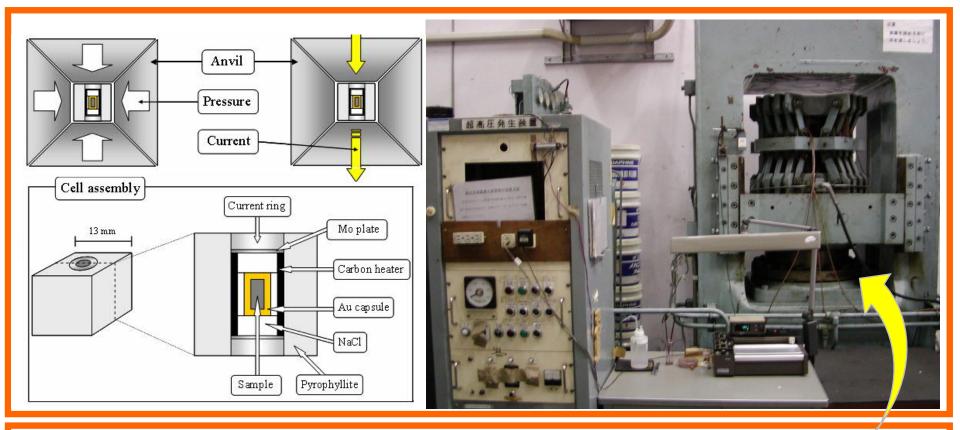
- Catenation (= chain-formation capability) typical for the carbon group (ref. organic chemistry)
- Catenation capability decreases: C > Si > Ge > Sn > Pb (after C the next in catenation capability is S)
- Also in the elemental form the C-C bond is strong, ref. carbon allotropes: graphite, diamond, fullerenes,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

 \rightarrow Boron nitride BN has in average the same number of valence electrons per atom as carbon \rightarrow C ja BN isoelectronic \rightarrow 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 conbustion 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 highpressure 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)



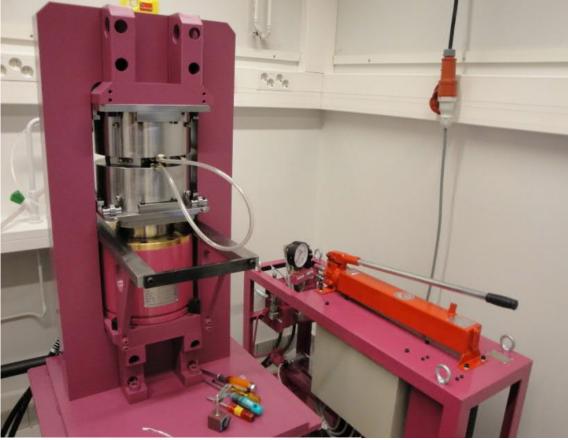
HIGH-PRESSURE SYNTHESIS

HP equipment

at Tokyo Tech

- 5 GPa = 50 000 atm
- 400 1200 °C
- 10 120 min
- 50 100 mg

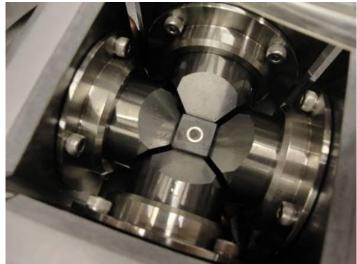
H. Yamauchi & M. Karppinen, Supercond. Sci. Technol. 13, R33 (2000).











HP equipment at Aalto

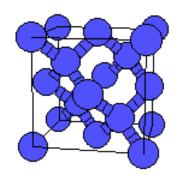
4 GPa & 25 GPa

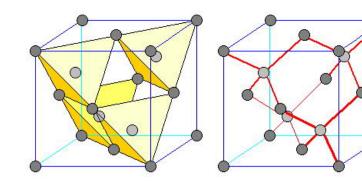
BORON NITRIDE

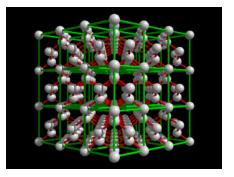
- Synthesis of boron nitride: $B_2O_3 + NH_3$ at 1000 °C \rightarrow graphite-type BN
- High-pressure high-temperature treatment \rightarrow diamond-type BN (so-called boratson)
- Also fullerene-type BN molecules known

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 \rightarrow diamond is the strongest material known
- Diamond-type BN is the second strongest material (ca. 50 % of the harness of diamond)
- Strong bonds \rightarrow high melting point (4100 °C)





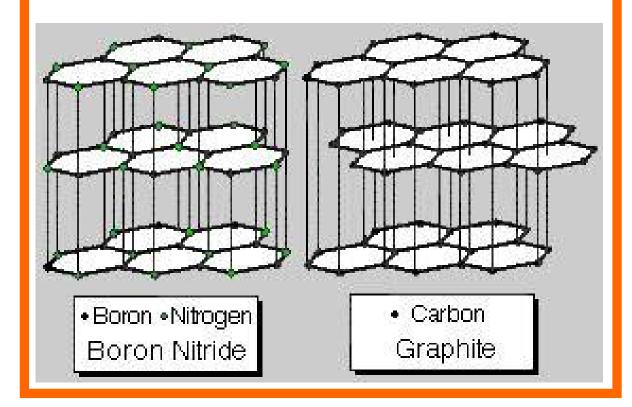


DIAMOND AS THERMAL CONDUCTOR & SEMICONDUCTOR

- 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 ≈ "impure C"
 - \rightarrow 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 \rightarrow p-type semiconductor
 - slight N excess \rightarrow n-type semiconductor

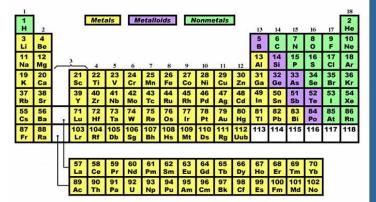
GRAPHITE STRUCTURE: C and BN

- 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</p>
- N (g), P (s; mp. 44 °C), As (s), Sb (s), Bi (s)
- N_2 gas (:N = N:) but C solid (4 x C-C)
- Melting points (°C): N -210, P 44, As subl. 615, Sb 631, Bi 271
 For metals/nonmetals m.p. decreases/inc

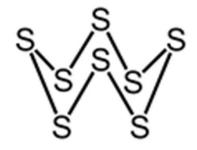


For metals/nonmetals m.p. decreases/increases in a group from up to down

- 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 "crowne" (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



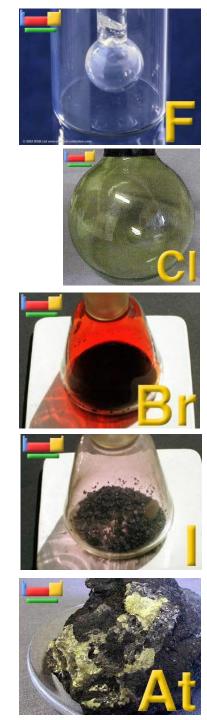




HALOGENS

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
CI ₂	-101	-34
Br ₂	-7	+60
۱ ₂	+114	+185
As .(rad. act)	+320	+337



FLUORINE VERSUS OTHER HALOGENS

- Atomic radius (Å): F 0.71, CI 0.99, Br 1.14, I 1.33
- Electronegativity: F 4.0, CI 3.0, Br 2.8, I 2.5, At 2.2
- Dissosiation energy (kJ/mol): F 155, CI 240, Br 190, I 149, At 116
- Oxidation states: F: -I
 CI: -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

- \rightarrow Large electron-electron repulsion in F₂
- ightarrow Small bond energy
- \rightarrow Highly reactive

Preparation of fluorine (from fuorite 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 CaF₂ mineral "Stink Spar" in Wölsendorf contains minute amounts of radioactive uranium inclusions
- Uranium constantly emits ionizing radiation which splits CaF₂ 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 F₂ on Earth by ¹⁹F-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
 - \rightarrow strong oxidizer
 - \rightarrow promotes high oxidation states for cations *
 - \rightarrow compounds ionic
 - \rightarrow strong hydrogen bonds

Cations often have higher oxidation states in oxides compared to fluorides,
 e.g. OsO₄ possible, but not OsF₈
 Reason: 8 F⁻ ions around Os⁸⁺ cation not possible !

NOBLE GASES: BASIC PROPERTIES

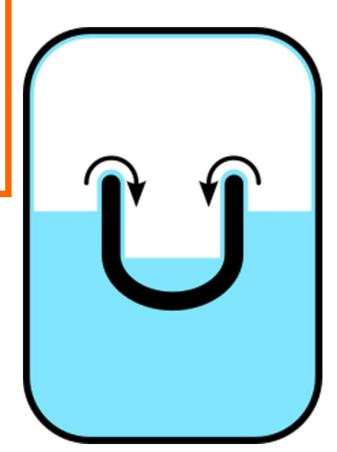
- Helium has the lowest known boiling point (-269 °C)
- Ionization energies (kJ/mol): He 2269, Ne 2079, Ar 1519, Kr 1349, Xe 1169, Rn 1036

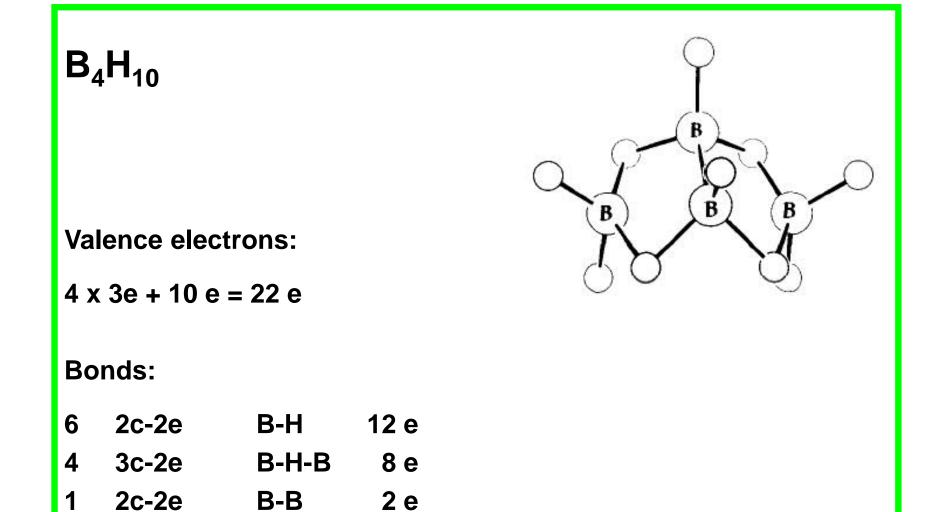
COMPOUNDS

- Bartlett 1962: $O_2(g) + PtF_6(g) \rightarrow [O_2^+][PtF_6^-](s)$
- Ionization energy of O₂ 1180 kJ/mol ≈ 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
- KMXeNaO₆ 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 → continuous movement → escape from the container
- Laws of classical mechanics do not work → quantum mechanics
- Ultrahigh thermal conductivity





B	5 H 11			ρ
Va	lence elec	trons:		$\mathcal{I} \cup \mathcal{I}$
5 >	3e + 11 e	= 26 e		0 0
Bo	onds:			
8	2c-2e	B-H	16 e	
3	3c-2e	B-H-B	6 e	
2	3c-2e	B-B-B	4 e	

