

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 (IN MyCourses/ZOOM)

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. Eu: Morina
U: Musikka & Seppänen

QUESTIONS: Lecture 10

- 1. Most stable oxidation state in acidic conditions: Mn, Fe, Co, Ni, Cu ?**
- 2. In which condition (acidic or basic) Cu^+ tends to disproportionate ?**
- 3. How many unpaired 3d electrons (oct./hs): Fe^{2+} , Fe^{3+} , Co^{2+} , Co^{3+} ?**
- 4. Which one of the iron oxides, FeO , Fe_3O_4 and Fe_2O_3 , is:**
 - mixed valent**
 - antiferromagnetic**
 - ferrimagnetic**
 - electrically conducting**
- 5. Give the abbreviated name for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$.**
- 6. Oxidation state of Cu in La_2CuO_4 , $\text{La}_2\text{CuO}_{4.1}$ and $(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{CuO}_4$?**
- 7. Are the above copper oxides superconducting ?**

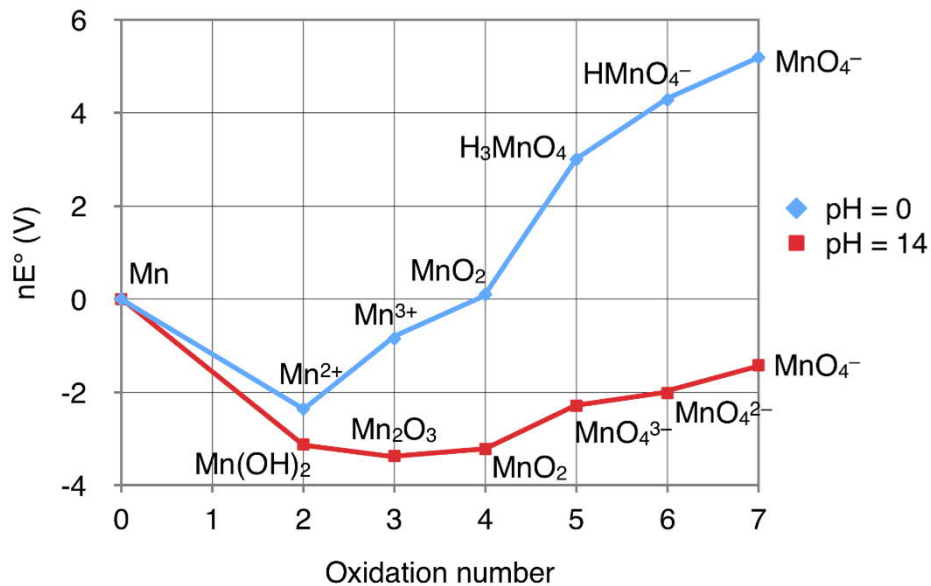
Group→	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	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
6	55 Cs	56 Ba	*	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
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			*	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	71 Lu
			**	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	103 Lr

Element	Symbol	Electronic Configuration
Scandium	Sc	$[\text{Ar}]3d^14s^2$
Titanium	Ti	$[\text{Ar}]3d^24s^2$
Vanadium	V	$[\text{Ar}]3d^34s^2$
Chromium	Cr	$[\text{Ar}]3d^54s^1$
Manganese	Mn	$[\text{Ar}]3d^54s^2$
Iron	Fe	$[\text{Ar}]3d^64s^2$
Cobalt	Co	$[\text{Ar}]3d^74s^2$
Nickel	Ni	$[\text{Ar}]3d^84s^2$
Copper	Cu	$[\text{Ar}]3d^{10}4s^1$
Zinc	Zn	$[\text{Ar}]3d^{10}4s^2$

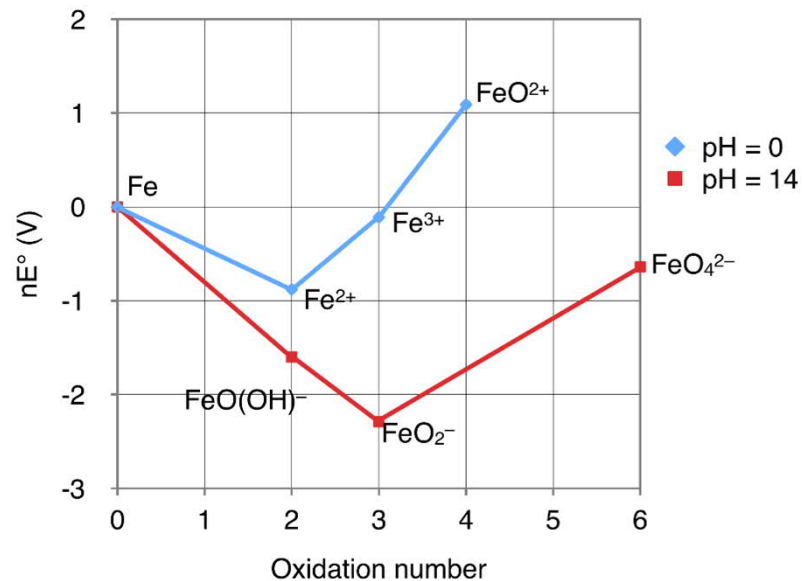
Element							
Sc							
Ti		+2	+3	+4			
V		+2	+3	+4	+5		
Cr		+2	+3	+4	+5	+6	
Mn		+2	+3	+4	+5	+6	+7
Fe		+2	+3	+4	+5	+6	
Co		+2	+3	+4	+5		
Ni		+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					

Mn, Fe, Co, Ni, Cu

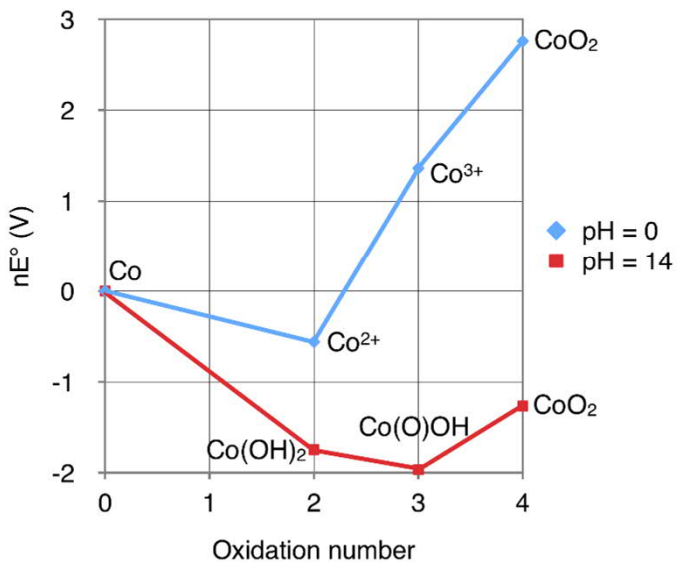
Frost diagram for manganese



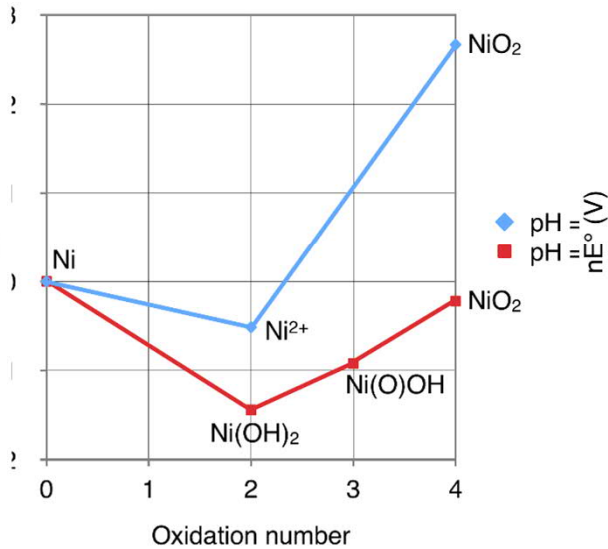
Frost diagram for iron



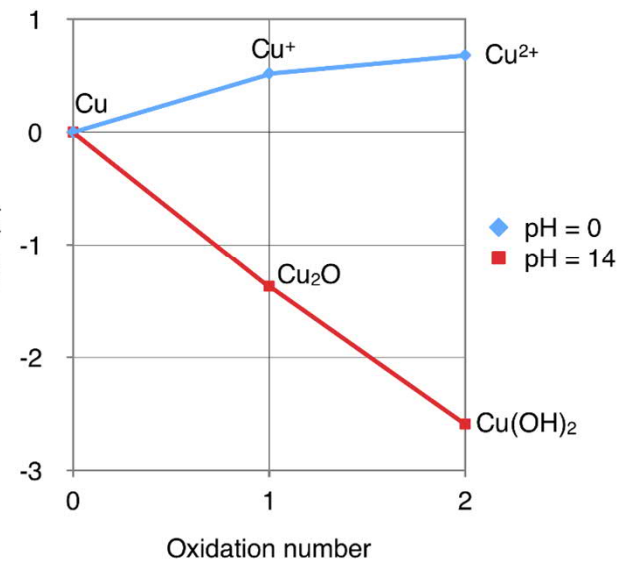
Frost diagram for cobalt



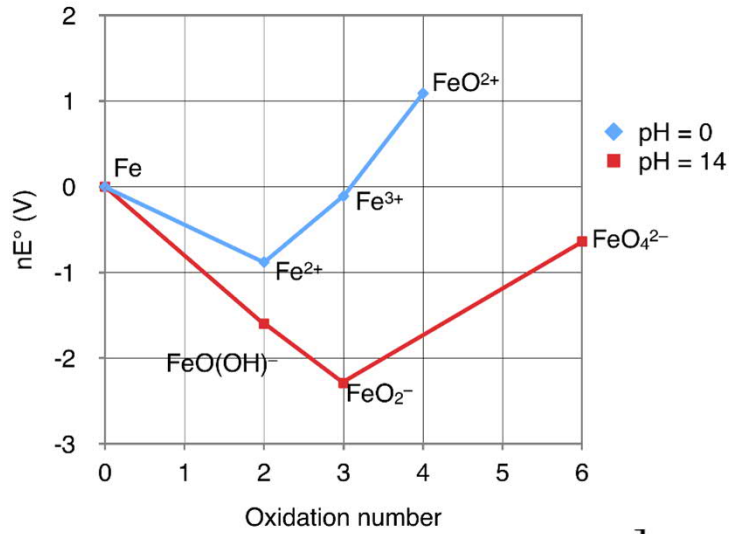
Frost diagram for nickel



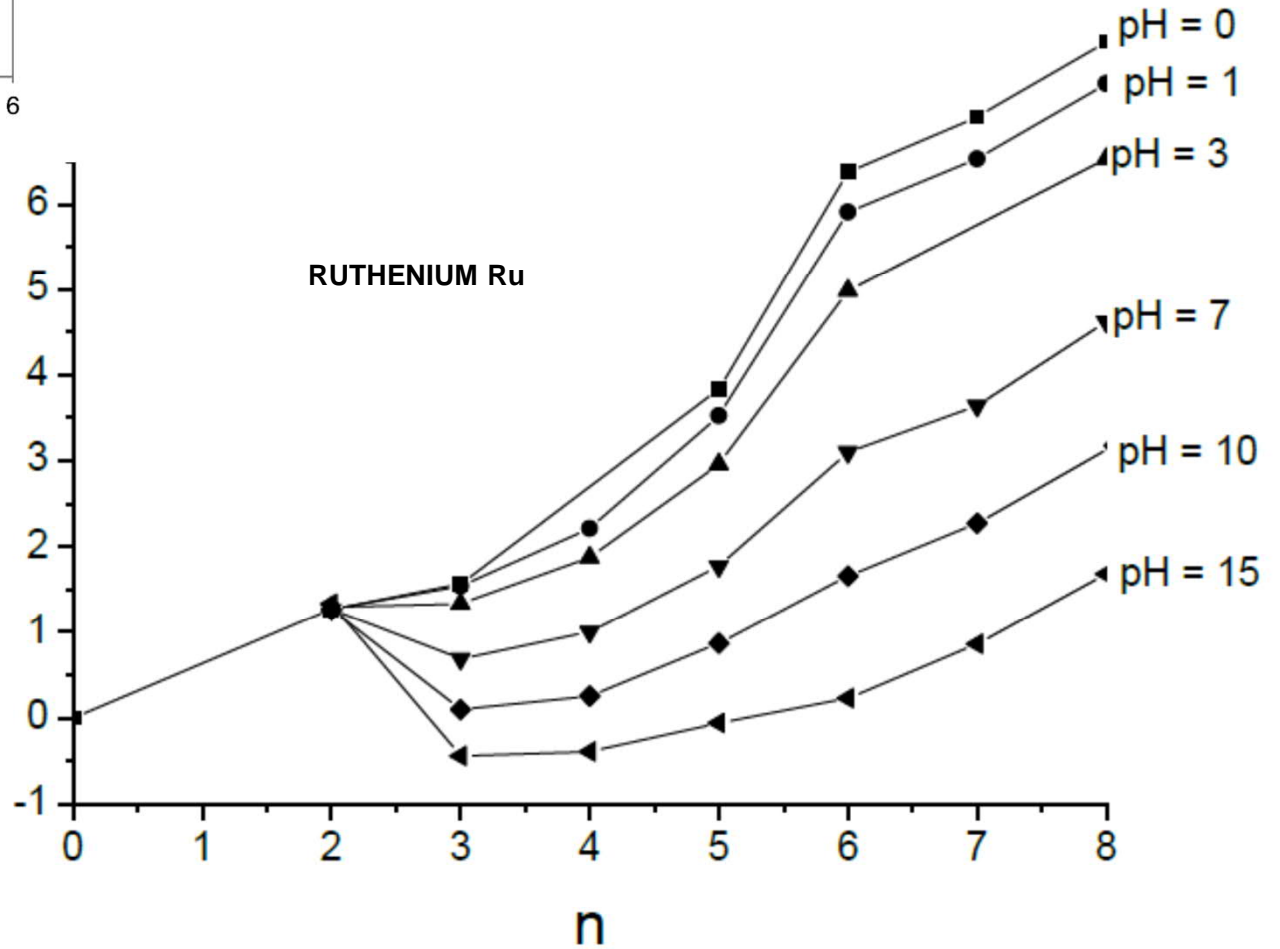
Frost diagram of copper



Frost diagram for iron



$\Delta G_r / \text{eV}$



Fe, Co, Ni & Platinum Metals (Ru, Os, Rh, Ir, Pd, Pt)

- **Horizontal relationships:**

- (1) Fe, Co, Ni, (2) light Pt metals, (3) heavy Pt metals

- **Vertical relationships:**

- (1) Fe, Ru, Os, (2) Co, Rh, Ir, (3) Ni, Pd, Pt

- **Electronegativities: Fe 1.8, Co 1.9, Ni 1.9, all Pt metals 2.2**

- **Oxides:**

- +II: (Fe,Co,Ni,Pd)O
- +II/III: (Fe,Co)₃O₄
- +III: (Fe,Co,Rh,Ir)₂O₃
- +IV: (Ru,Os,Rh,Ir,Pd,Pt)O₂
- +VIII: (Ru,Os)O₄

26	27	28	29	30
Fe	Co	Ni	Cu	Zn
44	45	46	47	48
Ru	Rh	Pd	Ag	Cd
76	77	78	79	80
Os	Ir	Pt	Au	Hg

OCTAHEDRAL COORDINATION

- Common for Mn, Fe, Co, Ni, Cu

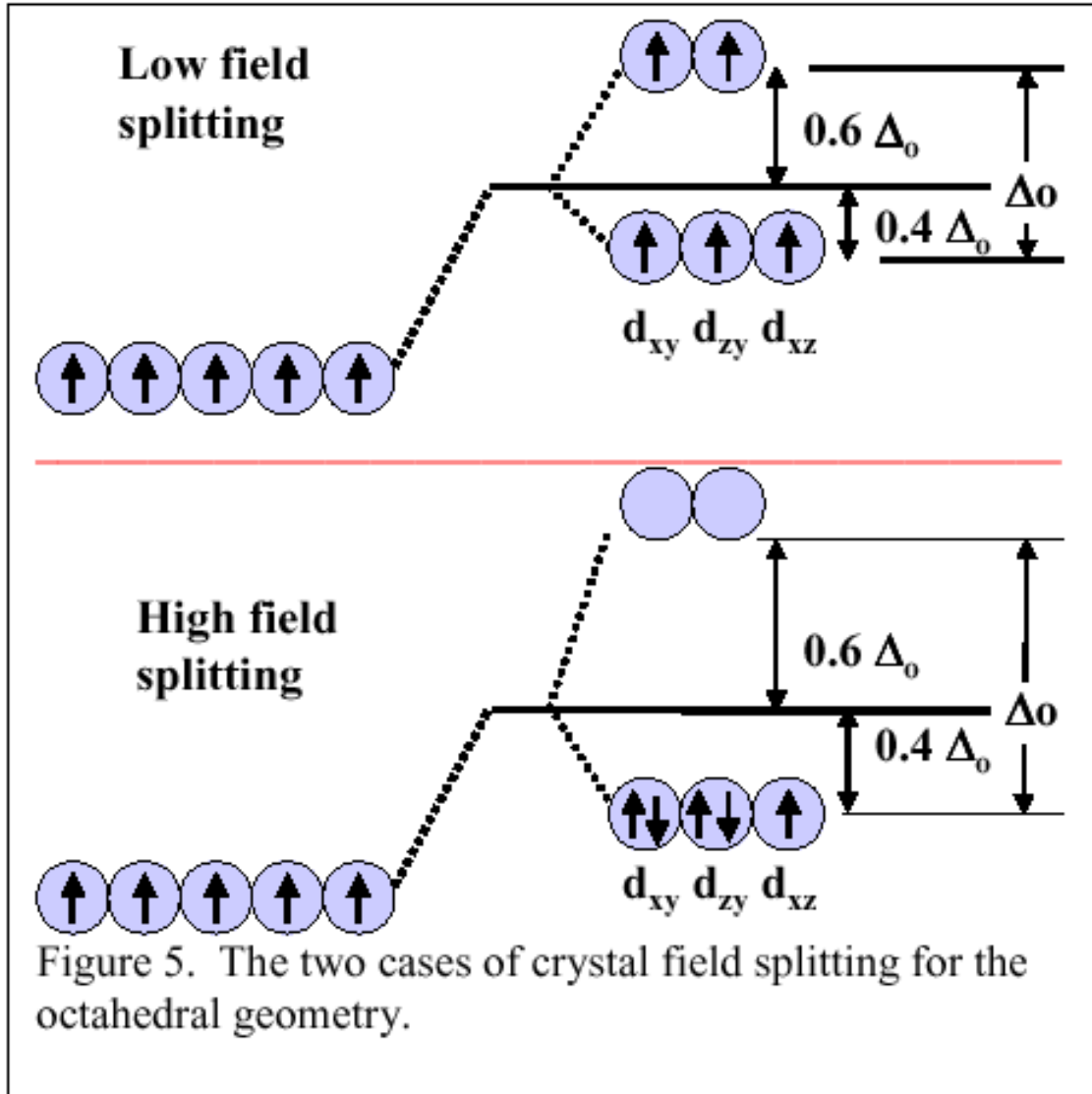
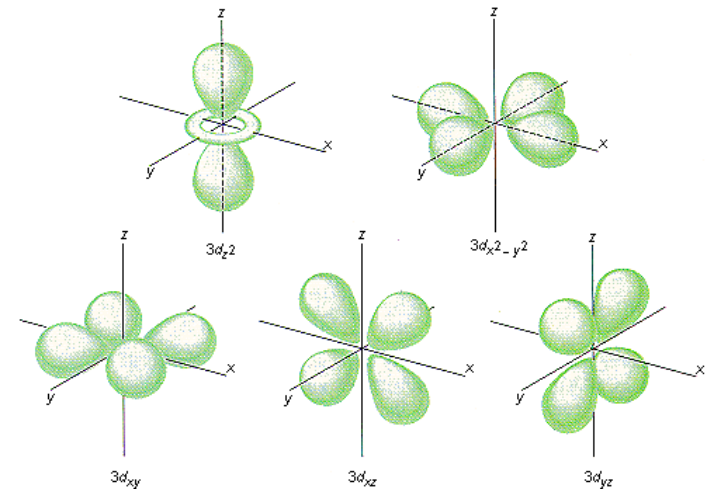


Figure 5. The two cases of crystal field splitting for the octahedral geometry.

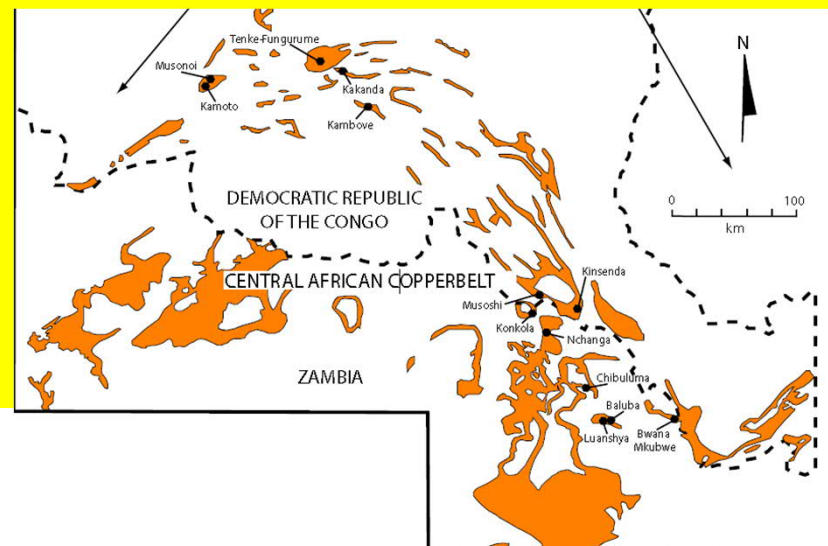
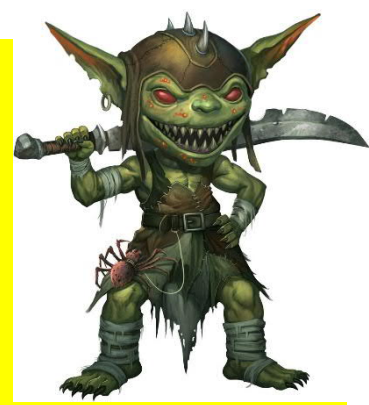


IRON COMPOUNDS

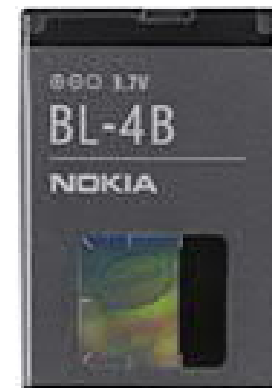
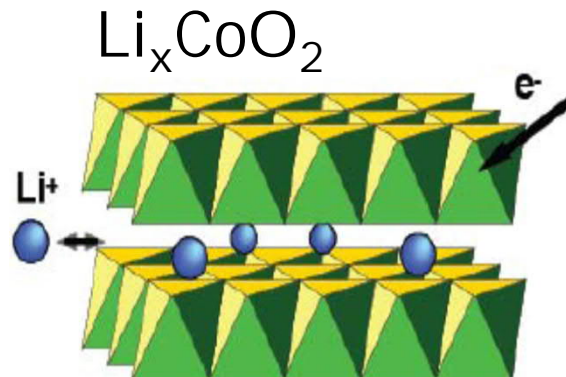
- Iron compounds mainly at the oxidation states +II and +III
- Fe(II) compounds tend to be oxidized to Fe(III) compounds in air
- Fe(II) compounds called **ferrous**, Fe(III) compounds **ferric**
- **ferrite** (magnetic spinel Fe(II/III) oxides) *versus* **ferrate** ($[\text{FeO}_4]^{4-}$, $[\text{FeO}_4]^{3-}$ & $[\text{FeO}_4]^{2-}$) !!!
(c.f. sulphite-sulphate, **manganite-manganate**, **cuprates** !!!)
- In rare compounds Fe occurs also at higher oxidation states, e.g. K_2FeO_4
- **Fe(IV) is a common intermediate in many biochemical oxidation reactions**
- ^{57}Fe Mössbauer spectroscopy is a powerful tool to investigate oxidation states and other bonding properties of Fe in its compounds
- Many important **mixed-valence Fe(II)/Fe(III) compounds**, such as magnetite Fe_3O_4
- Main **industrial-scale** products/intermediates: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and FeCl_3

COBALT

- Cobalt-based blue pigments (cobalt blue; CoAl_2O_4) have been used since ancient times in jewelry, paints and glass
- Ancient miners used the German name *kobold ore* (*goblin ore*) for some blue-pigment producing minerals
- In 1735 metallic cobalt was reduced from these ores (first metal discovered since ancient times) and named *kobold*
- Nowadays only minor amounts of Co are produced from Co ores, e.g. cobaltite CoAsS , the main production being as a by-product of Cu and Ni mining
- The copper belt in Africa (Congo, Zambia) is the main source of cobalt
- Co is used as a metal in magnetic, wear-resistant, high-strength alloys
- Cobalt $\rightarrow \text{LiCoO}_2$!
- OXIDES:
 - CoO : green, rock-salt, AFM ($T_N = 291 \text{ K}$)
 - Co_3O_4 : blue, spinel, AFM ($T_N = 40 \text{ K}$)
 - Co_2O_3 : black



In Kokkola:
 Outokumpu → OMG → FreeportCobalt → Umicore



For Chemical Applications



- Cobalt Acetate
- Cobalt Carbonate
- Cobalt Hydroxide
- Cobalt Oxide
- Cobalt Sulfate
- Coarse Grade Cobalt Powder
- Recycling

For Pigment and Ceramic Applications



- Ceramic Pigments*
- Cobalt Oxide
- Plastic Pigments*
- Cobalt Oxide
 - Cobalt Hydroxide
- Glass Pigments*
- Cobalt Oxide

For Powder Metallurgy Applications



- S-Series Cobalt Powder
- R-Series Cobalt Powder
- Granulated Cobalt Powder
- Coarse Grade Cobalt Powder

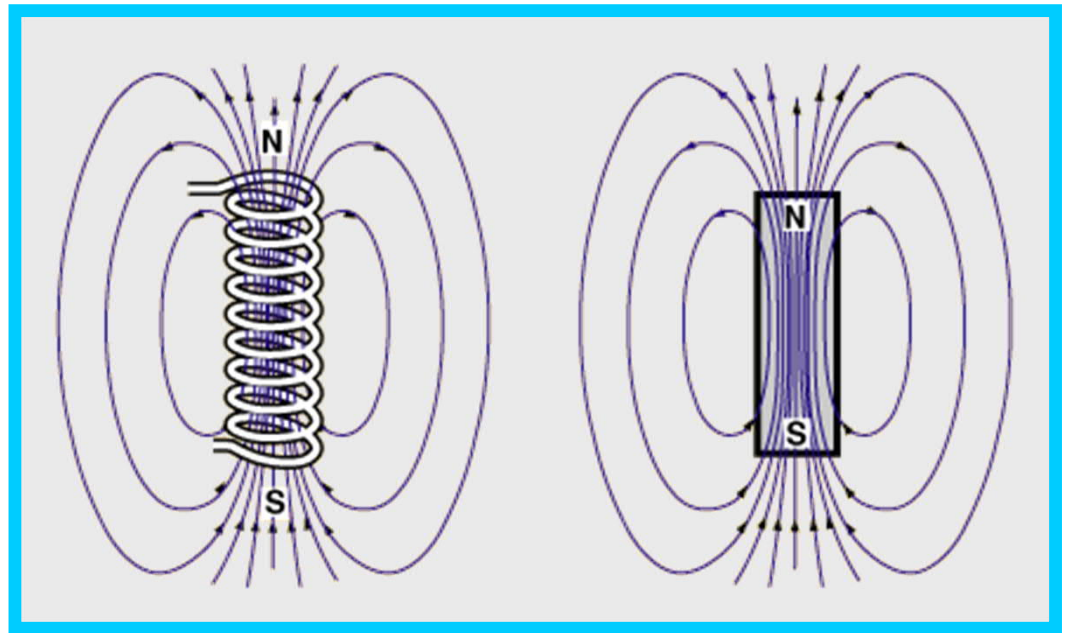
For Battery Applications



- Precursors*
- Battery Grade Cobalt Oxide
 - Mixed Metal Hydroxides
- Battery Materials*
- Fine Cobalt Powder
 - Cobalt Hydroxide
- Raw Materials*
- Battery Grade Cobalt Powders
 - Cobalt Sulfate

COPPER

- **Known since 5000 BC:**
lat. *Cuprum* (Cyprus; oldest mining places, 3000 BC)
- **Occurrence: 68 ppm; mainly as sulphides**
- **Electronegativity: 1.9**
- **Similarities with alkali metals: $d^9s^2 \rightarrow d^{10}s^1$**
however, Cu smaller, denser, less reactive, more electronegative, and forms coordination compounds
- **Binary oxides: Cu_2O , CuO**
- **Compounds with higher oxidation states:**
 LaCuO_3 , K_3CuF_6 , KCuO_2 , high- T_c superconducting oxides
- **How to stabilize the high oxidation states for transition metals:**
 - combine with the most electronegative anions
 - combine with the most electropositive cations
 - use highly oxidizing synthesis conditions/high pressures
- **Enzyme reactions: $\text{Cu(I)} \rightarrow \text{Cu(III)}$**



MAGNET

- Magnet: solid/bar/coil that creates a magnetic field
- Electromagnet: electric current
- Permanent magnet: unpaired electrons
- Magnets have two poles: *S (south)* and *N (north)*
- Same-type poles repel each other and opposite-type poles attract each other

Magnetic Field Ranges

Field Size

Example

Field Size

Example

850T



the strongest Destructive Pulsed magnet

$4 \times 10^{-1} \text{T}$



lodestone

Mineral magnetite

60T



60 T long Pulse magnet

$3 \times 10^{-1} \text{T}$



Household refrigerator magnet

33T



33T continuous field magnet

10^{-2}T



Surface of Sun

2T



MRI machine

10^{-4}T



Near Household Wiring

$4 \times 10^{-1} \text{T}$



Stereo Speaker Magnets

$3 \times 10^{-5} \text{T}$



Surface of Earth

$3 \times 10^{-10} \text{T}$



Produced by Human Body

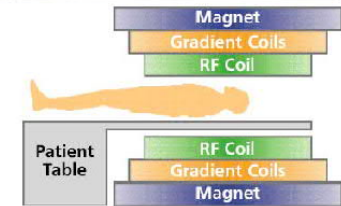
Superconducting Magnets

- Solenoid as in conventional electromagnet.
- But once current is injected, power supply turned off, current and magnetic field stays forever...
...as long as $T < T_c$



Magnets for MRI

- Magnetic Resonance Imaging typically done at 1.5 T
- Superconducting magnet to provides static magnetic field
- Spatial resolution of positions of tracer atomic nuclei.



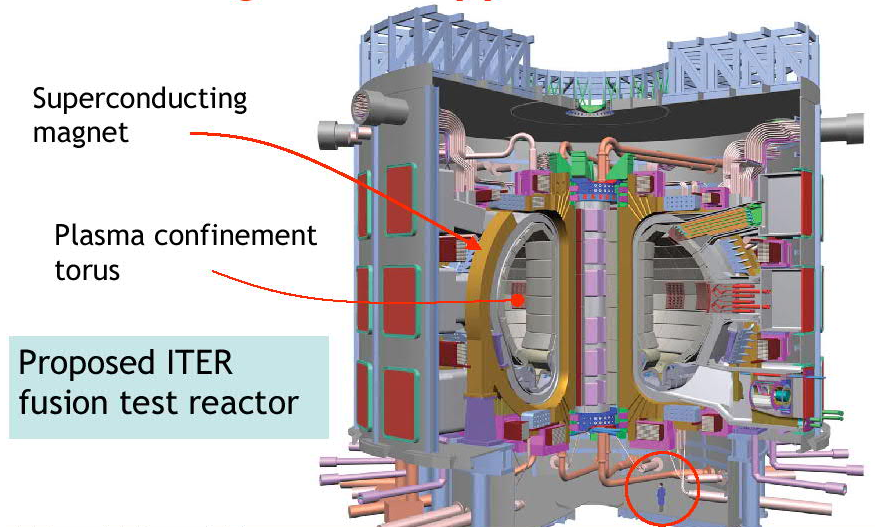
900 MHz NMR (UW Chemistry)



21.7 T field



Large scale applications



MAGNETIC SUSCEPTIBILITY

Magnetization (M):

magnetic field induced in sample in external magnetic field (H)

Magnetic susceptibility: $\chi = M / H$

DIAMAGNET: $\chi < 0$ (very small)

PARAMAGNET: $\chi > 0$ (very small)

FERROMAGNET: $\chi > 0$ (very large)

ANTIFERROMAGNET: $\chi > 0$ (small)

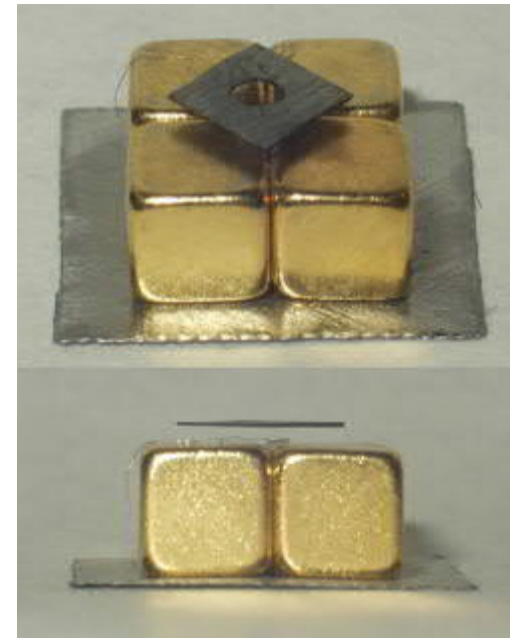
FERRIMAGNET: $\chi > 0$ (large)

DIAMAGNETISM (“NON-MAGNETISM”)

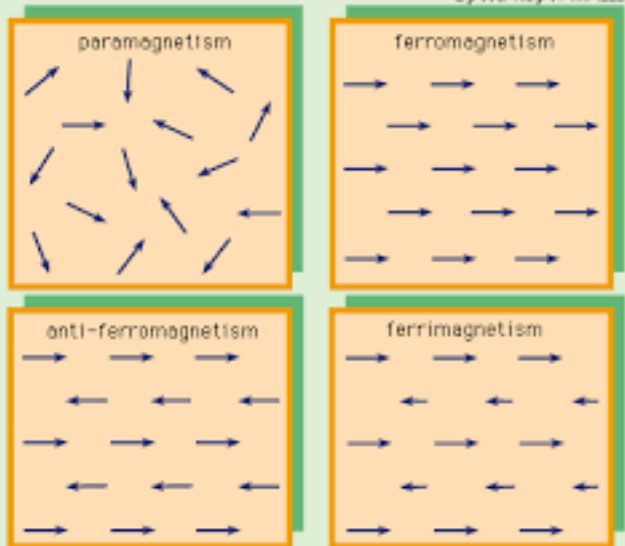
- All materials are diamagnetic
- Due to the movement of all electrons in atoms
- Diamagnetic material repels external field ($\chi < 0$)
- Diamagnetism is of several orders of magnitude weaker phenomenon compared to other phenomena of magnetism

(material is said to be diamagnetic only if it does not show other forms of magnetism)

- e.g. water: $\chi = -9.05 \times 10^{-6}$
- So-called pyrolytic carbon is a particularly strong diamagnet (χ up to -400×10^{-6})
- Superconductors are perfect diamagnets (in their superconducting state): $\chi = -1$
- Superconductors perfectly repel external fields (Meissner effect)



Pyrolytic carbon bar levitates above permanent magnet



RT MAGNETISM OF PURE ELEMENTS

1 H 2 He

 Ferromagnetic Antiferromagnetic

 Paramagnetic Diamagnetic

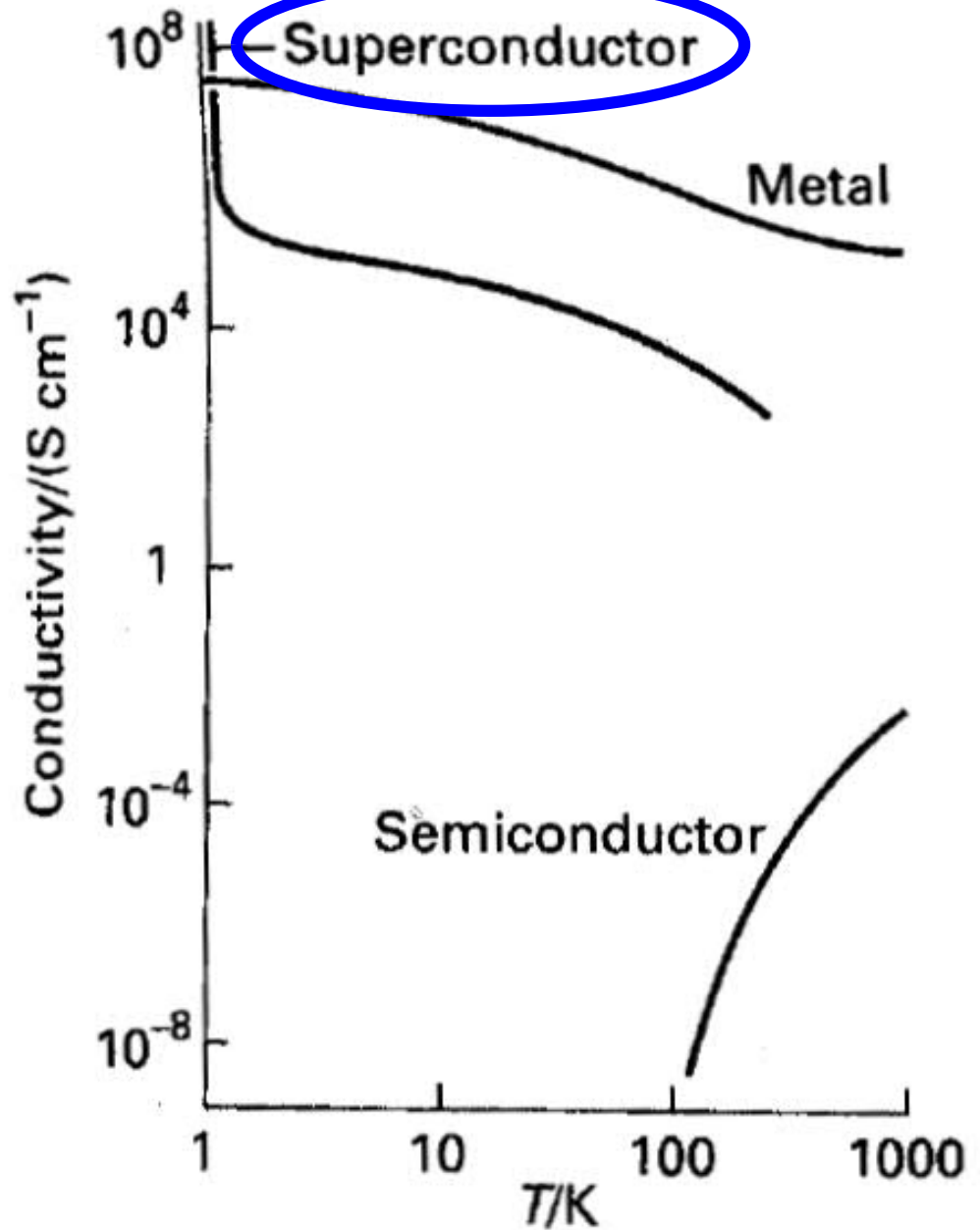
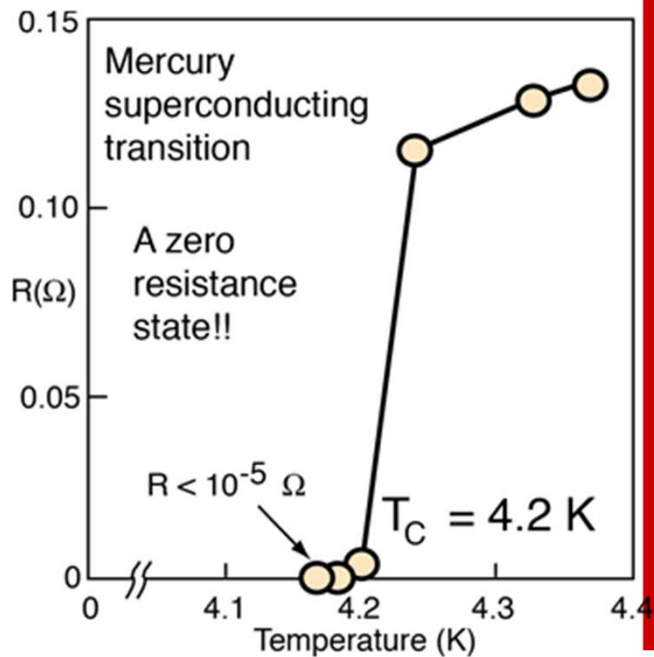
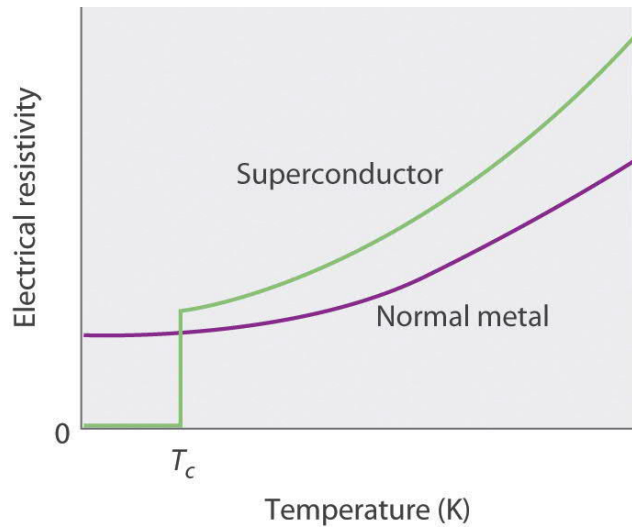
3	4											5	6	7	8	9	10														
Li	Be											B	C	N	O	F	Ne														
11	12											13	14	15	16	17	18														
Na	Mg											Al	Si	P	S	Cl	Ar														
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr														
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54														
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe														
55	56	57		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86													
Cs	Ba	La		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn													
87	88	89	↓																												
Fr	Ra	Ac																													
																		58	59	60	61	62	63	64	65	66	67	68	69	70	71
																		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Ferromagnets: T_c [K]

iron	1043
cobalt	1404
nickel	628
gadolinium	289
erbium	32
dysprosium	155
barium ferrite	720
strontium ferrite	720
Alnico	1160
Alumel	436
Mutamel	659
Permalloy	869
Trafoperm	1027
NdFeB	580
SmCo ₅	990
Sm ₂ Co ₁₇	1070
CrO ₂	390
CuAlMn ₃	???
La _x Ca _{1-x} B ₆	900
MnAs	318
MnBi	633
polymerized C ₆₀	~500

Antiferromagnets: T_N [K]

CoCl ₂	25
CoF ₂	38
CoO	291
chromium	475
Cr ₂ O ₃	307
erbium	80
FeCl ₂	70
FeF ₂	79 - 90
FeO	198
FeMn	490
α -Fe ₂ O ₃	953
MnF ₂	72 - 75
MnO	122
MnSe	173
MnTe	310 - 323
NiCl ₂	50
NiF ₂	78 - 83
NiFeO	180
NiO	533 - 650
TiCl ₃	100
UCu ₅	15
V ₂ O ₃	170



SUPERCONDUCTIVITY

Superconductivity

1911 Kamerlingh-Onnes: $\rho = 0$
- Hg with $T_c = 4.2$ K

"Meissner effect"

1933 Meissner and Ochenfeld:
 $\chi = B/H < 0 \rightarrow$ levitation

High- T_c superconductivity

1986: Bednorz and Müller
- $(\text{La,Ba})_2\text{CuO}_4$ with $T_c = 30 \sim 40$ K

Present record in T_c :

138 K for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$



Nobel 1913



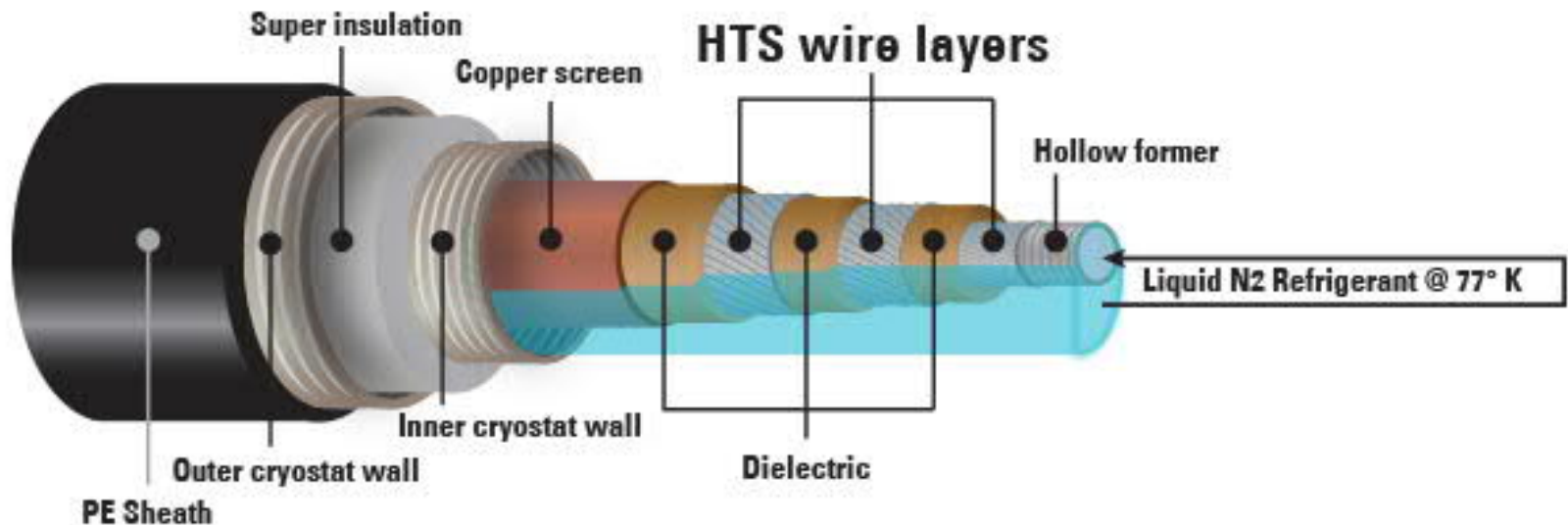
Nobel 1987



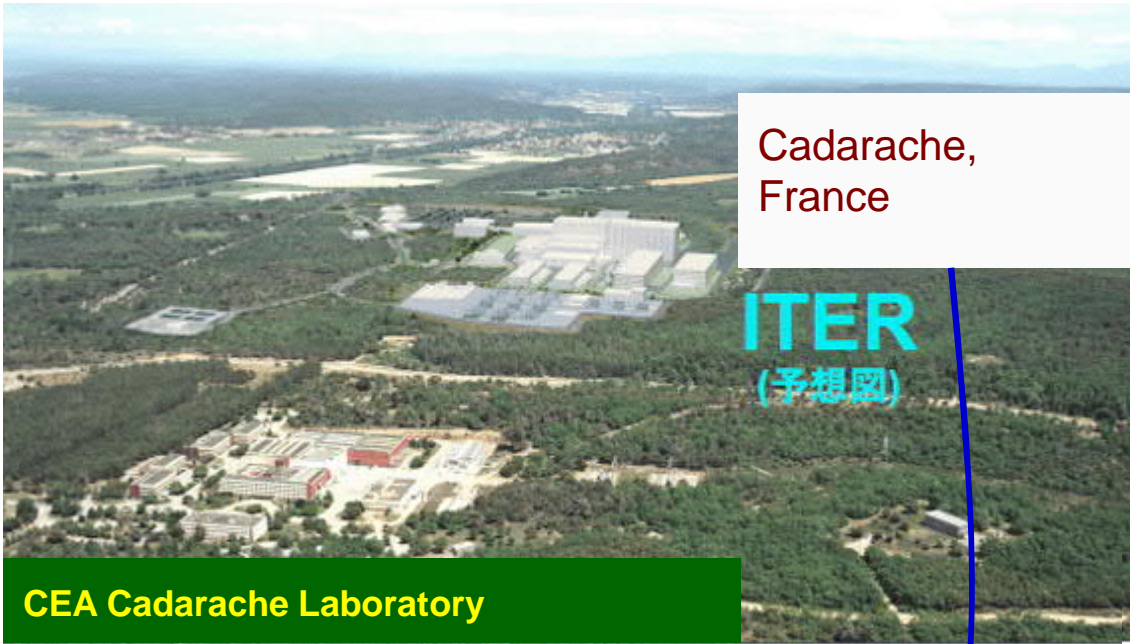
SUPERCONDUCTING POWER CABLES

- Normal Cu wires: 20% energy waste
- High-temperature superconductor cables introduced since 2000s
- In 2008 the longest cable installed in Long Island, New York: transmitting up to 574 megawatts of electricity (enough to power 300,000 homes)

Typical HTS Cable Configuration

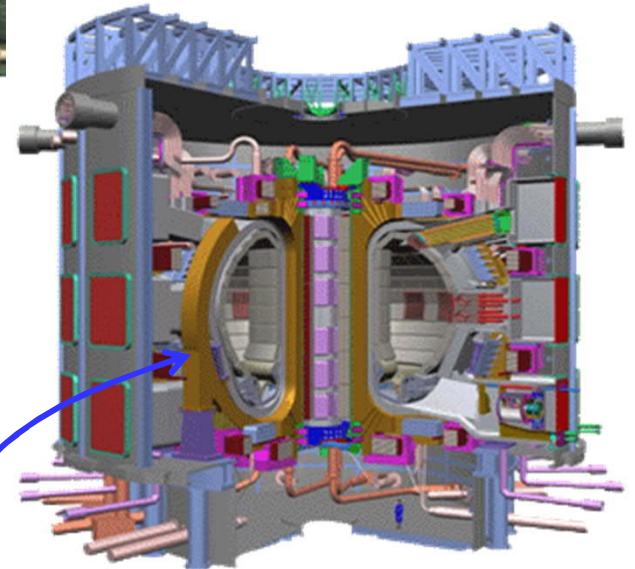


ITER: International Thermonuclear Experimental Reactor

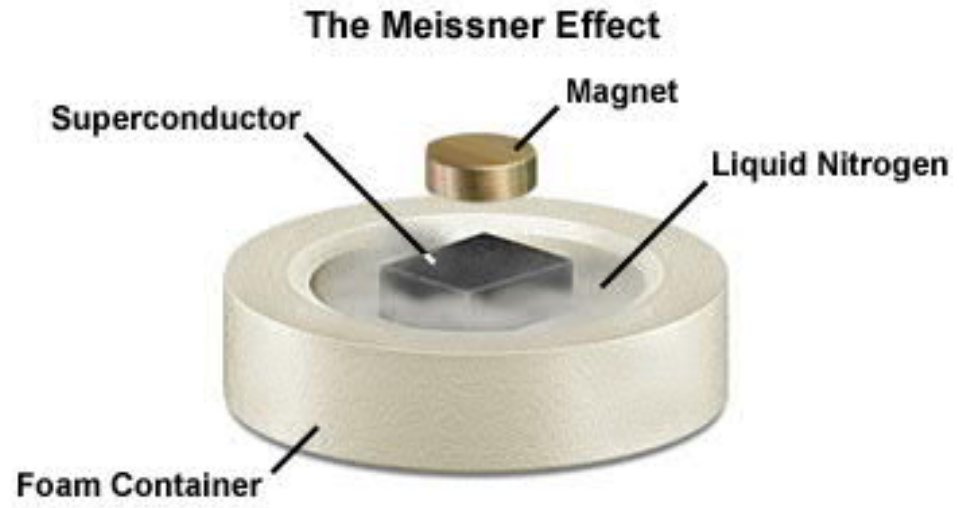
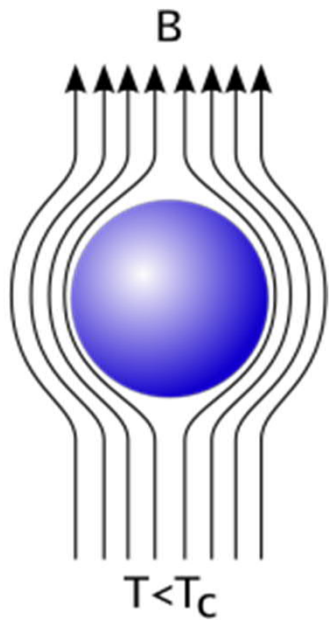
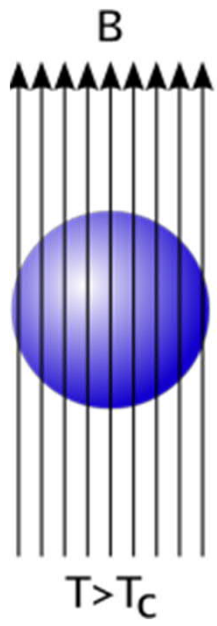


since October, 2007

**Nuclear Fusion
Reactor**



Superconducting Magnets





Super-Maglev Train

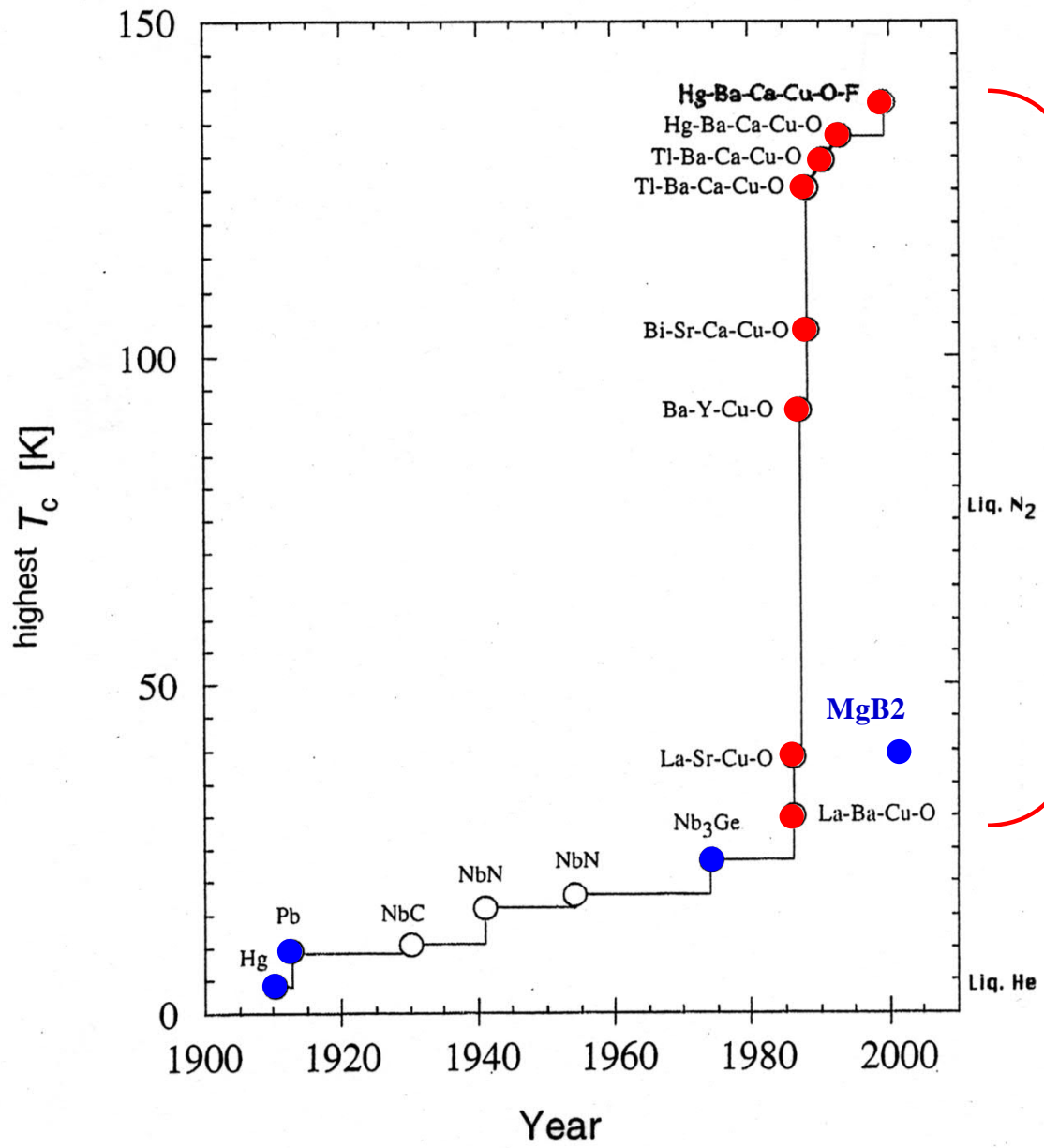
- 603 km / hour
- Test line 42.8 km

Superconducting Elements

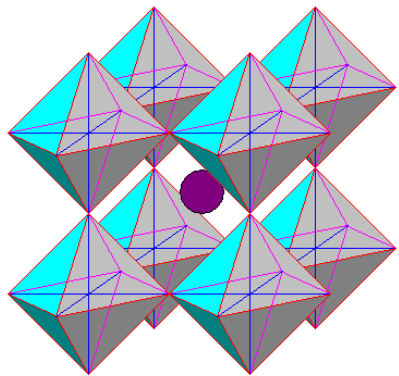
1	1	H																	2	He																
2	3	Li	4	Be																	5	B	6	C	7	N	8	O	9	F	10	Ne				
3	11	Na	12	Mg																	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar				
4	19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
5	37	Rb	38	Sr	39	Y	40	Zr	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
6	55	Cs	56	Ba	57	La	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
7	87	Fr	88	Ra	89	Ac	104	Rf	105	Ha	106	Sg	107	Bh	108	Hs	109	Mt	110	Ds	111	Rg	112	Uub												

- In Bulk at Ambient Pressure
- At High Pressure
- In Modified Form

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cr	Es	Fm	Md	No	Lr

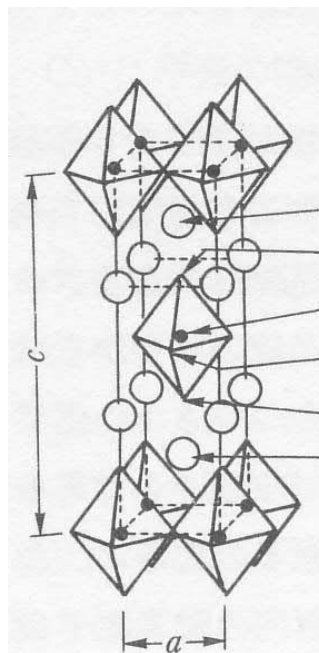


"HTSC"



Perovskite CaTiO_3

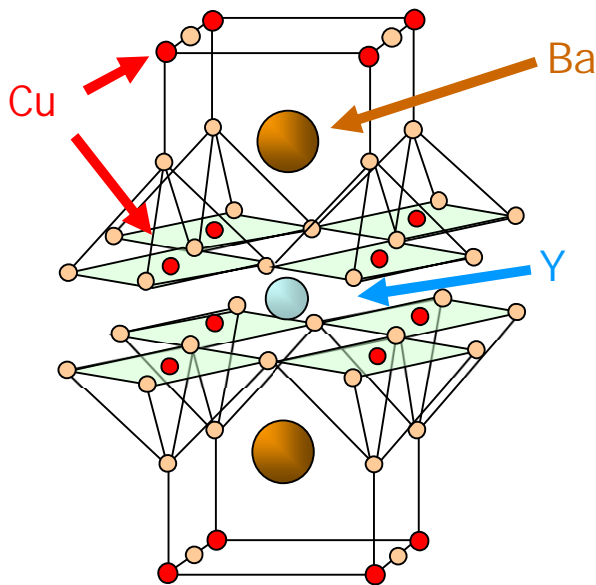
Crystal Structures of High- T_c Superconductive Copper Oxides



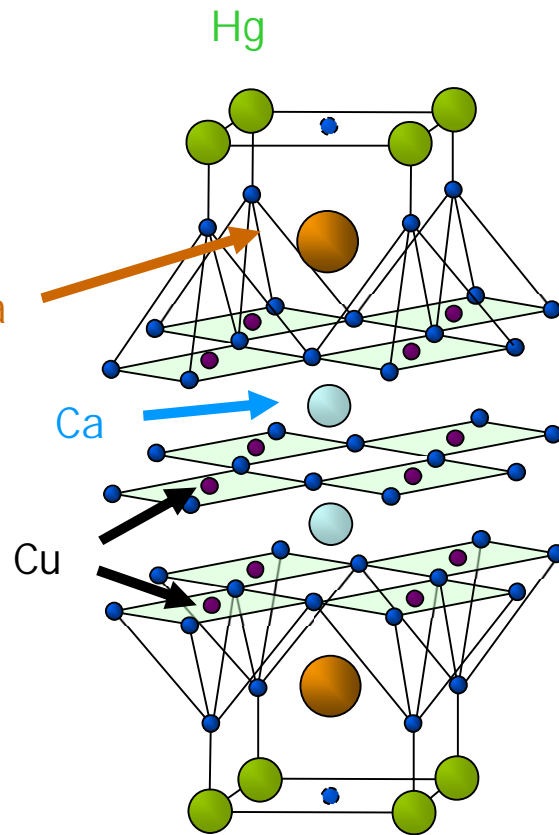
(La, Ba)
O
Cu
O
O
(La, Ba)



$T_c \approx 35 \text{ K}$

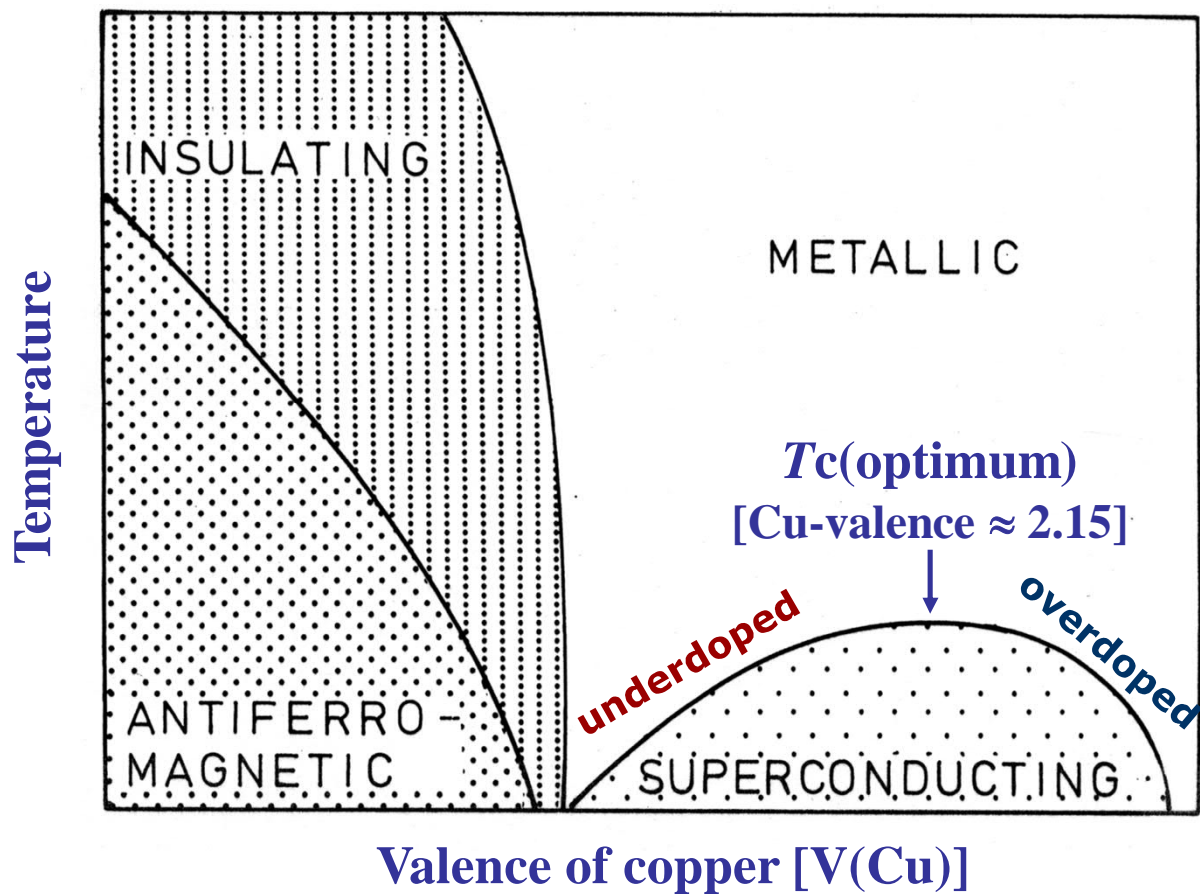


$T_c \approx 92 \text{ K}$



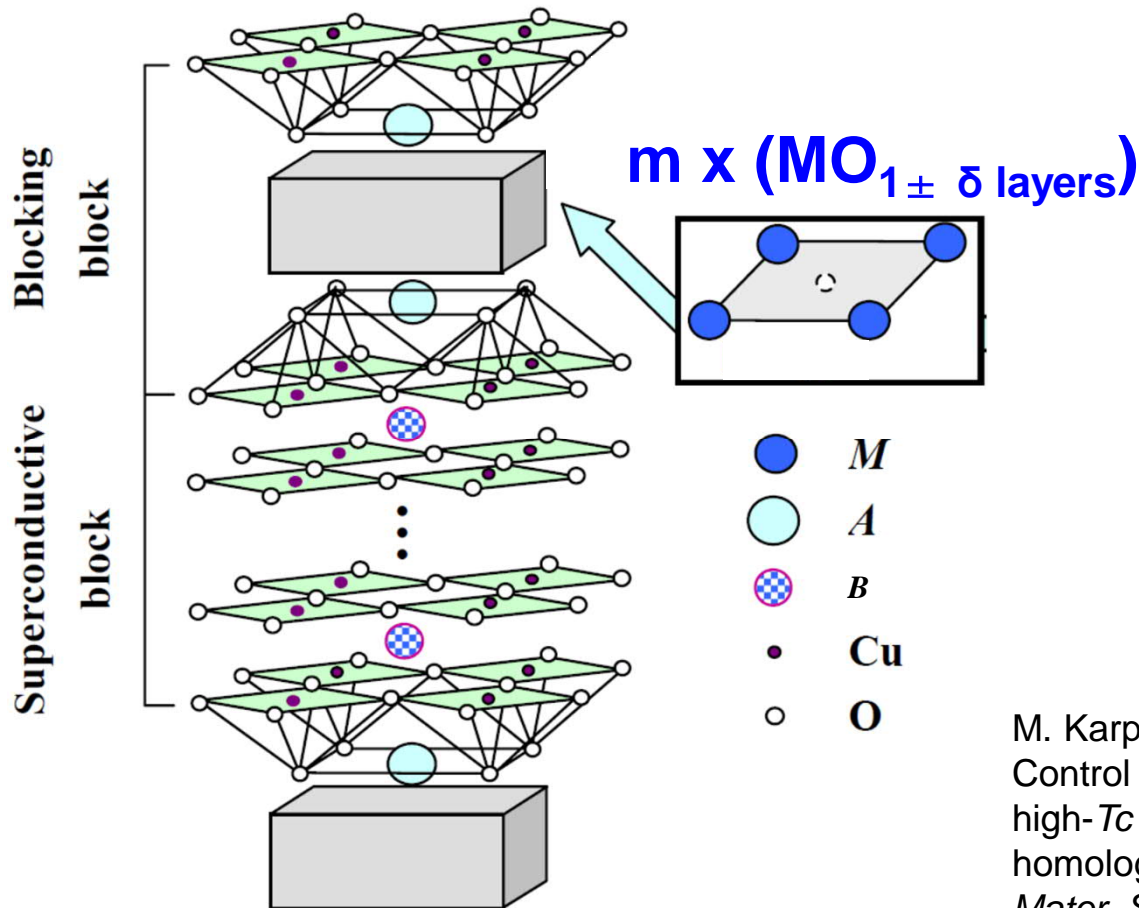
$T_c \approx 135 \text{ K}$

Phase Diagram of HTSC

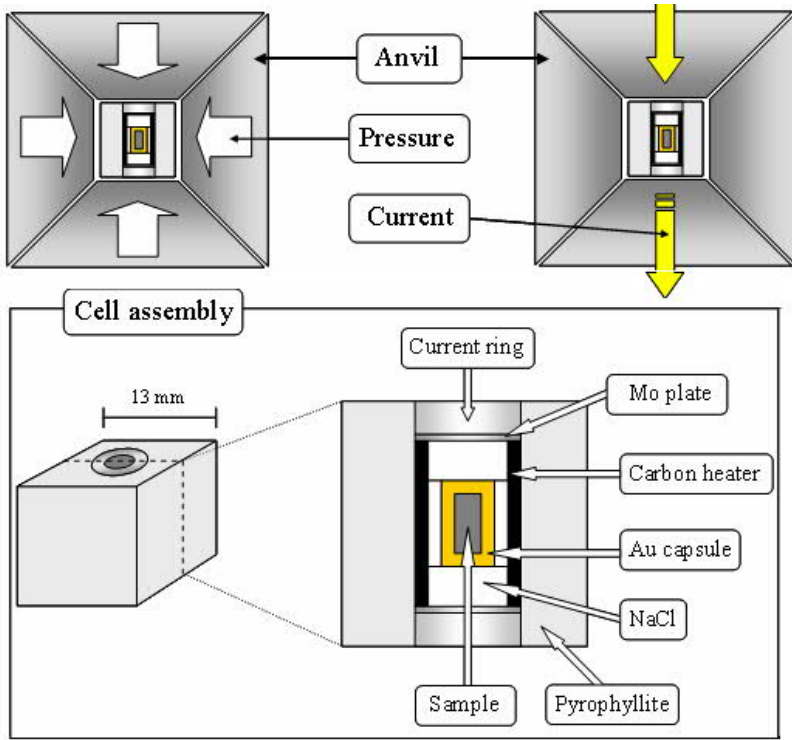


GENERAL FORMULA

- $M_m A_2 B_{n-1} Cu_n O_{m+2+2n \pm \delta}$
- $M-m2(n-1)n$
- **HOMOLOGOUS SERIES: M, m, A and B fixed, n varies**



M. Karppinen & H. Yamauchi,
Control of the charge inhomogeneity and
high- T_c superconducting properties in
homologous series of multi-layered copper oxides,
Mater. Sci. Eng. R **26**, 51-96 (1999).



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).

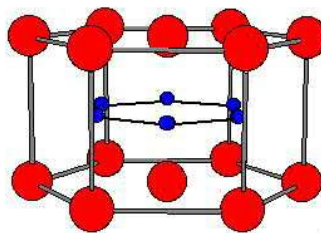


$$M - m2(n-1)n$$

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	57 to 71	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	89 to 103	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt										

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	71 Lu
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	103 Lr

Akimitsu 2001:
MgB₂



Hosono 2001:
[La(O,F)][FeAs]

