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 & Perovskites & Metal Complexes & MOFs & MLD
9.	Wed	28.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
10.	Fri	30.09.	Mn, Cu, Ru
11.	Mon	03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Fri	07.10.	Lanthanoids + Actinoids & Luminescence
13.	Mon	10.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
14.	Wed	12.10.	Resources of Elements & Rare/Critical Elements
15.	Fri	14.10.	Inorganic Materials Chemistry Research

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

QUESTIONS: Lecture 13 (SAME as Lecture 10 Questions !)

1. Most stable oxidation state(s) for: Mn, Fe, Co, Ni, Cu ?

2. How many unpaired 3d electrons in metals: Mn, Fe, Co, Ni, Cu ?

3. Propose a (simple-minded) reason why Mn is not ferromagnetic.

4. Propose a (simple-minded) reason why Cu is not ferromagnetic.

5. How many unpaired 3d electrons (oct./hs): Fe^{2+}, Fe^{3+} ?

6. Which one(s) of the iron oxides, FeO, Fe_3O_4 and Fe_2O_3, is/are:
   - mixed valent
   - antiferromagnetic
   - ferrimagnetic
   - electrically conducting

PRESENTATION TOPICS/SCHEDULE

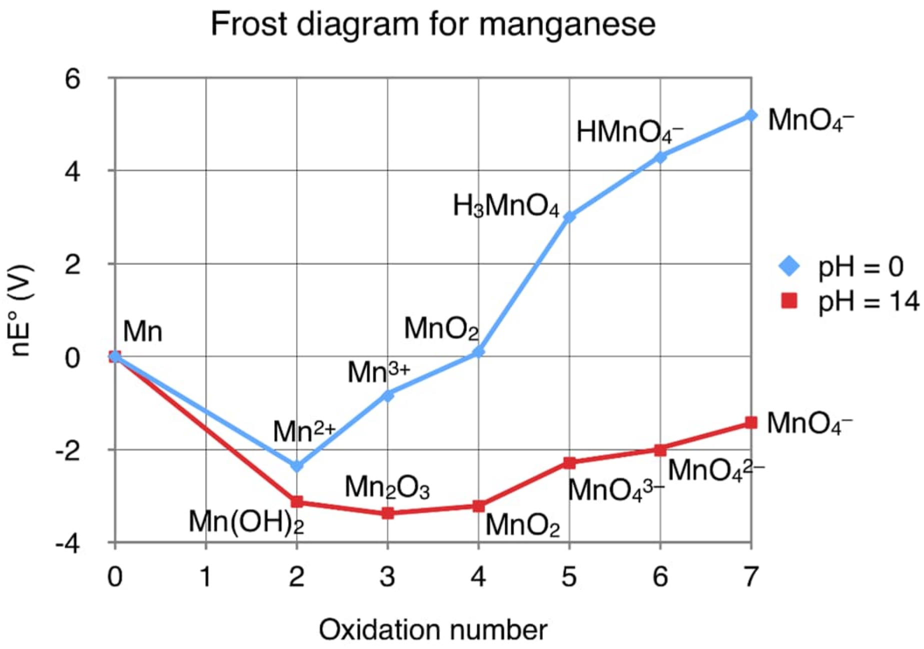
Fri	16.09.	Zn:	Rautakorpi, Stenbrink & Hyvärinen
Mon	26.09.	Nb:	Souza, Rahikka & Tong
Wed	28.09.	Mo:	Alimbekova & Tran (Nhi)
		Ti:	Mäki & Israr
Fri	30.09.	Mn:	Tao & Song (Zonghang)
		Cu:	Marechal, Weppe & Ishtiaq
		Ru:	Järvinen & Verkama
Fri	07.10.	Eu:	Bardiau, Wolfsberger & Klingerhöfer
		Nd:	Helminen, Olsio & Keskimaula
Mon	10.10.	U:	Airas & Holopainen
Wed	12.10.	Co:	Song (Yutong) & Lone
		In:	Antila & Wallius
		Te:	Peussa & Heylen

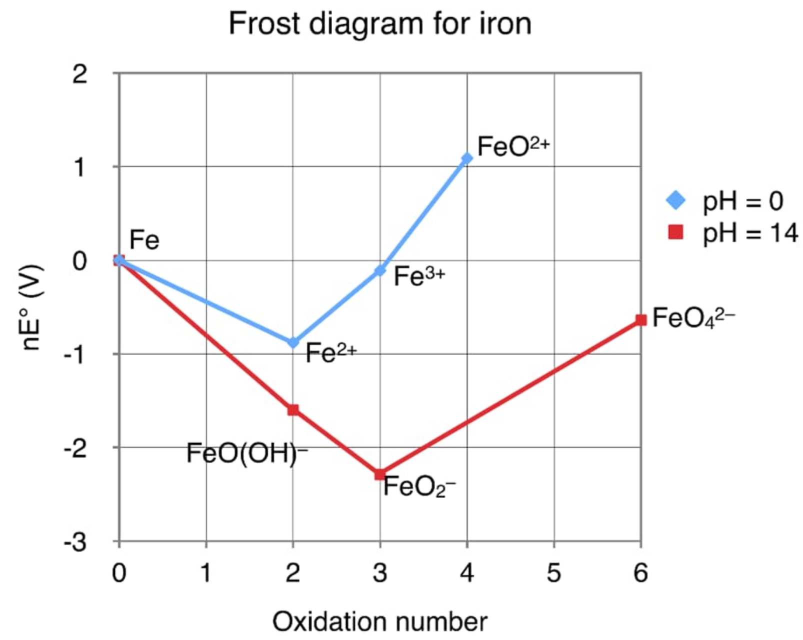
Group → / ↓Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 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	

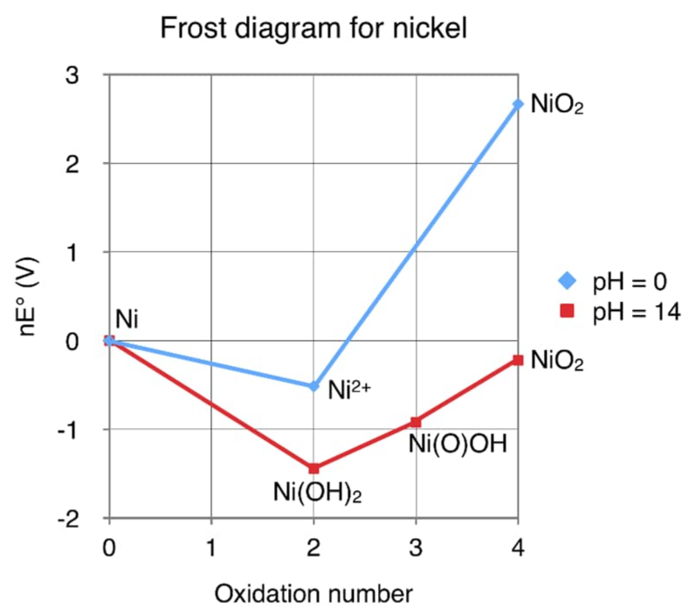
Element	Symbol	Electronic Configuration
Scandium	Sc	$[Ar]3d^{1}4s^{2}$
Titanium	Ti	$[Ar]3d^{2}4s^{2}$
Vanadium	V	$[Ar]3d^{3}4s^{2}$
Chromium	Cr	$[Ar]3d^{5}4s^{1}$
Manganese	Mn	$[Ar]3d^{5}4s^{2}$
Iron	Fe	$[Ar]3d^{6}4s^{2}$
Cobalt	Co	$[Ar]3d^{7}4s^{2}$
Nickel	Ni	$[Ar]3d^{8}4s^{2}$
Copper	Cu	$[Ar]3d^{10}4s^{1}$
Zinc	Zn	$[Ar]3d^{10}4s^{2}$

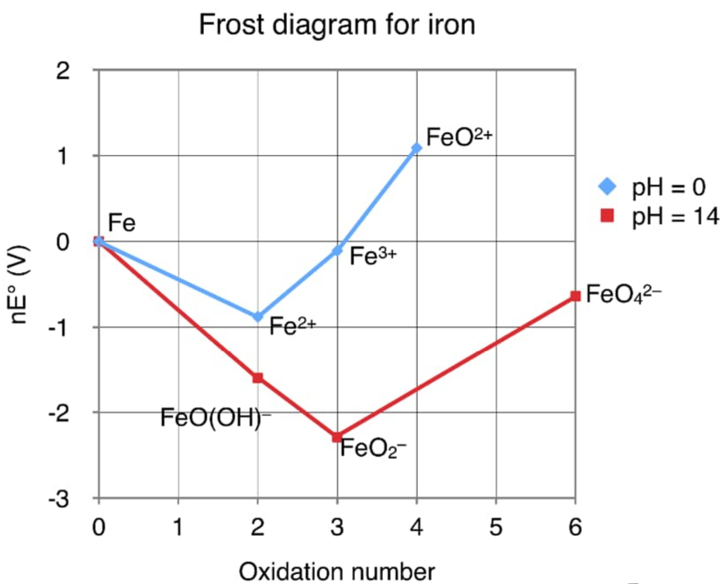
Element							
Sc			**+3**				
Ti		+2	+3	**+4**			
V		+2	+3	**+4**	**+5**		
Cr		+2	**+3**	+4	+5	+6	
Mn		**+2**	+3	+4	+5	+6	+7
Fe		**+2**	**+3**	+4	+5	+6	
Co		**+2**	**+3**	+4	+5		
Ni		**+2**	+3	+4			
Cu	+1	**+2**	+3				
Zn		**+2**					

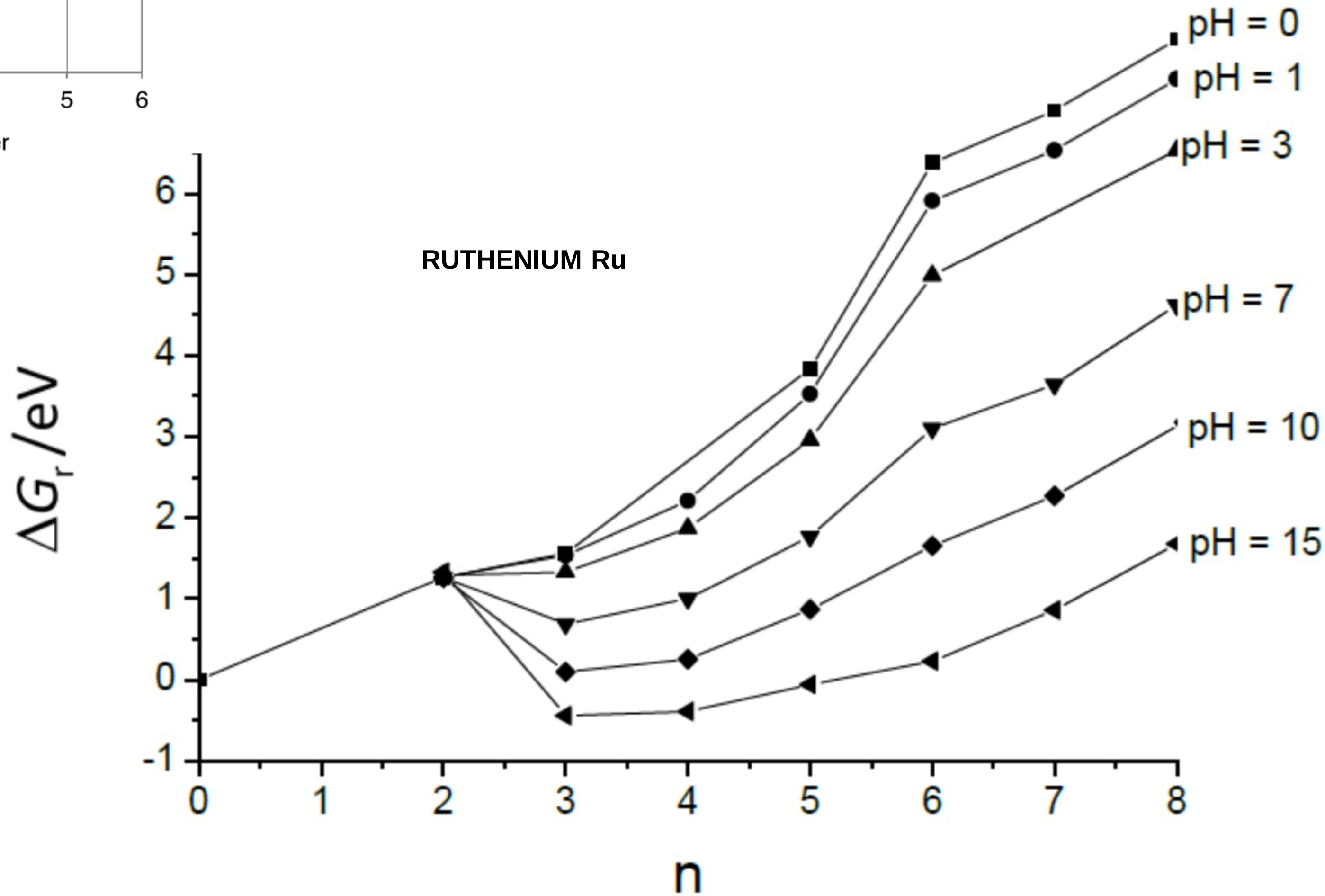
Mn, Fe, Co, Ni, Cu


Frost diagram for manganese
nE° (V)
Oxidation number
pH = 0
pH = 14
Mn
Mn2+
Mn3+
MnO2
H3MnO4
HMnO4−
MnO4−
Mn(OH)2
Mn2O3
MnO2
MnO43−
MnO42−
MnO4−


Frost diagram for iron
nE° (V)
Oxidation number
pH = 0
pH = 14
Fe
Fe2+
Fe3+
FeO2+
FeO(OH)−
FeO2−
FeO42−

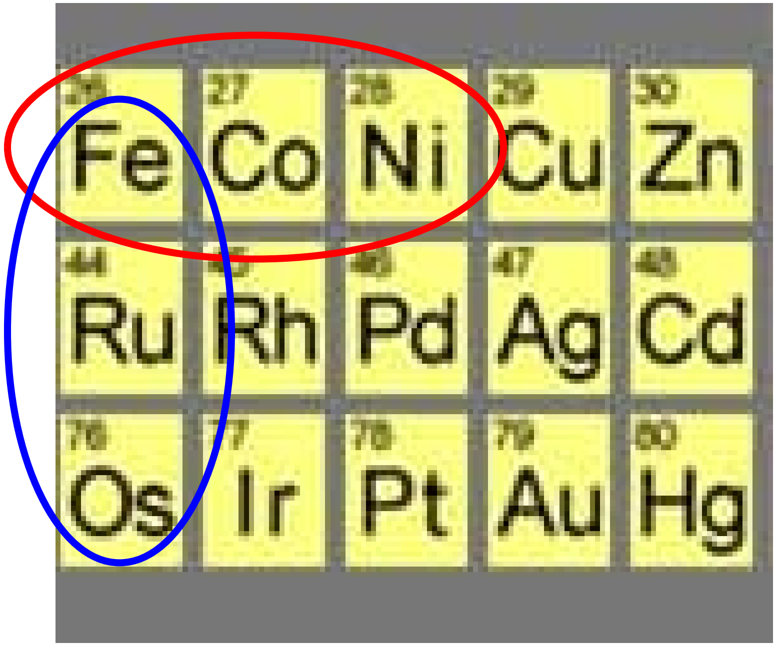

Frost diagram for nickel
nE° (V)
Oxidation number
pH = 0
pH = 14
Ni
Ni2+
NiO2
Ni(OH)2
Ni(O)OH
NiO2


Frost diagram for iron
nE° (V)
Oxidation number
pH = 0
pH = 14
Fe
Fe2+
Fe3+
FeO2+
FeO(OH)⁻
FeO2⁻
FeO42⁻
2
1
0
-1
-2
-3
0
1
2
3
4
5
6


RUTHENIUM Ru
ΔGr /eV
n
pH = 0
pH = 1
pH = 3
pH = 7
pH = 10
pH = 15
6
5
4
3
2
1
0
-1
0
1
2
3
4
5
6
7
8

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: $(Fe,Co)_3O_4$
  - +III: $(Fe,Co,Rh,Ir)_2O_3$
  - +IV: $(Ru,Os,Rh,Ir,Pd,Pt)O_2$
  - +VIII: $(Ru,Os)O_4$



OCTAHEDRAL COORDINATION

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

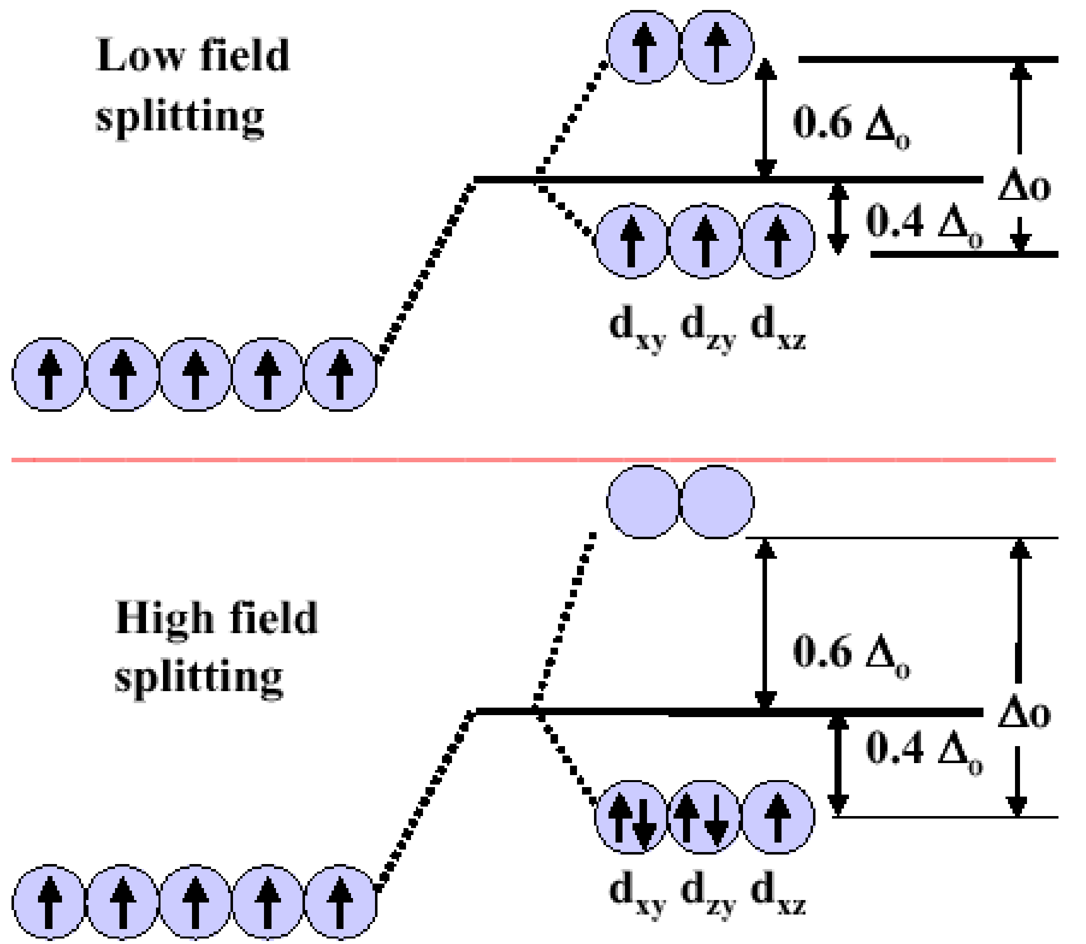
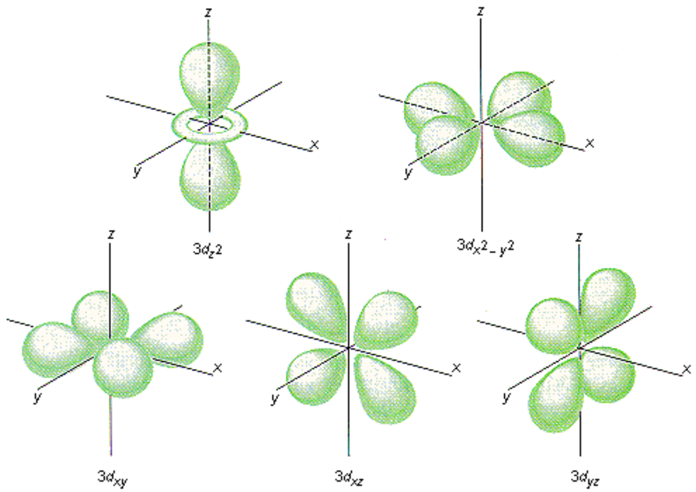


Figure 5. The two cases of crystal field splitting for the octahedral geometry.



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
- **Ferrous Fe(II)** compounds & **Ferric Fe(III)** compounds
- **Ferrite** (magnetic spinel Fe(II/III) oxides) &
  Ferrate (highest oxidation state $[FeO_4]^{4-}$, $[FeO_4]^{3-}$ & $[FeO_4]^{2-}$) **!!!**
  (c.f. sulphite-sulphate, **manganite-manganate**, **supercond. cuprates**)
- Most common oxides: FeO and Fe_2O_3 (hematite) antiferromagnetic, Fe_3O_4 ferrimagnetic & electrically conducting, **mixed-valence Fe(II)/Fe(III)**
- In rare compounds Fe occurs also at higher oxidation states, e.g. K_2FeO_4
- **Fe(IV) is common intermediate in biochemical oxidation reactions**
- ^{57}Fe Mössbauer spectroscopy is a powerful tool to investigate oxidation states and other bonding properties of Fe in its compounds
- Main **industrial-scale** products/intermediates: $FeSO_4 \cdot 7H_2O$ and $FeCl_3$

COPPER

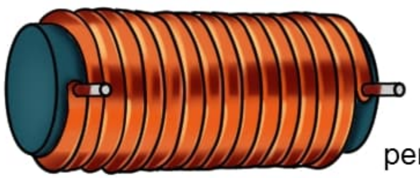
- **Known since 5000 BC:**

  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: Cu(I) $\rightarrow$ Cu(III)**



MAGNETISM in BRIEF

- Magnet: solid that creates a magnetic field

  (1) Electromagnet: electric current (through a coil)

  (2) Permanent magnet: unpaired electrons

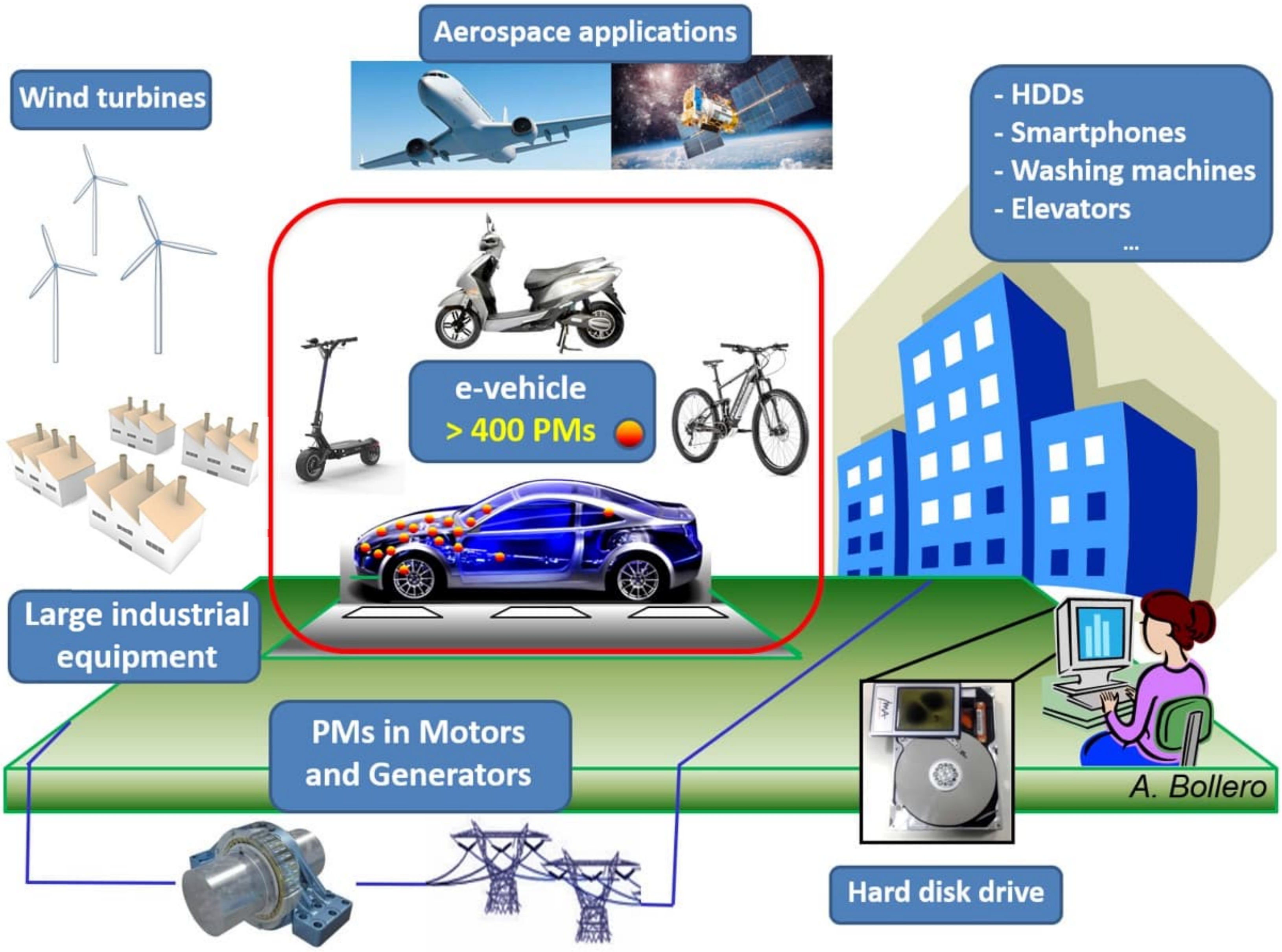
<u>PERMANENT MAGNETS</u>

- Each electron is a small magnet due to its spin
- In most materials, the countless electrons have randomly oriented spins, leaving no magnetic effect on average
- In some rare magnetic materials, many of the electron spins are aligned in the same direction, such that they create a net magnetic field
- There is also an additional (minor) magnetic field that results from the electron's orbital motion (cf. electromagnets)
- Magnetic properties of solids depend on:

  - electron configuration

  - crystal structure

APPLICATIONS of PERMANENT MAGNETS



APPLICATIONS of ELECTROMAGNETS

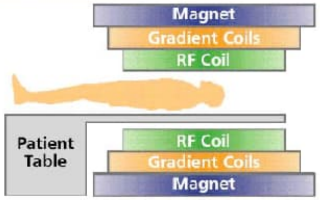
Superconducting Magnets

- 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

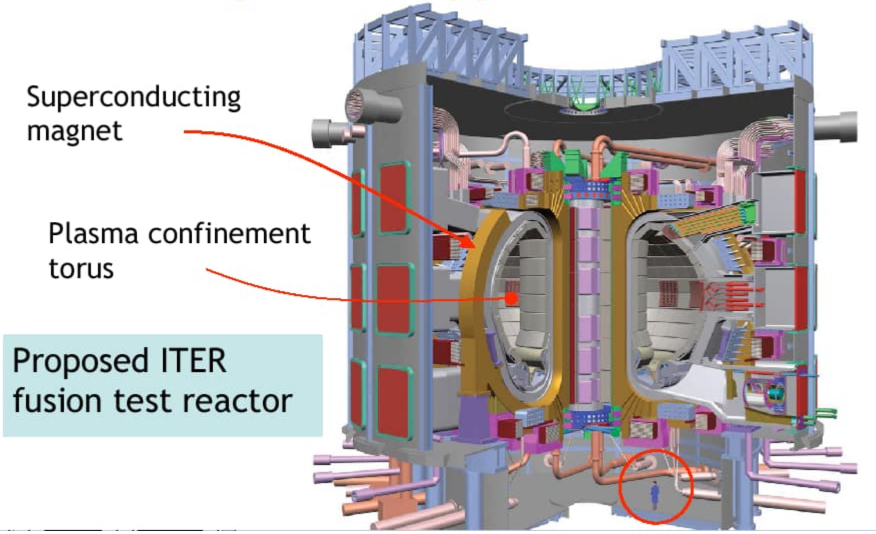
- Magnetic Resonance Imaging typically done at 1.5 T
- Superconducting magnet to provides static magnetic field
- Spatial resolution of positions of tracer atomic nuclei.



900 MHz NMR (UW Chemistry)

21.7 T field

Large scale applications

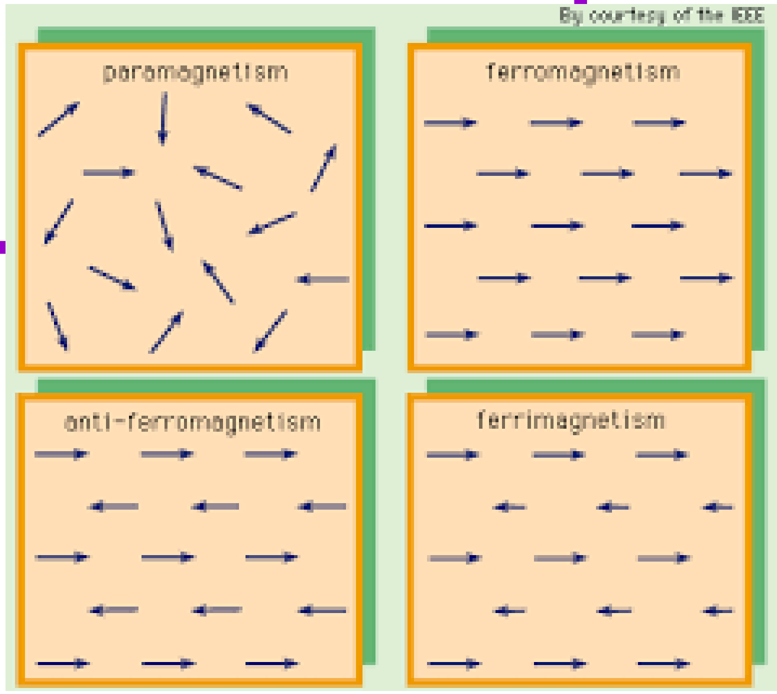


MAGNETIC SUSCEPTIBILITY

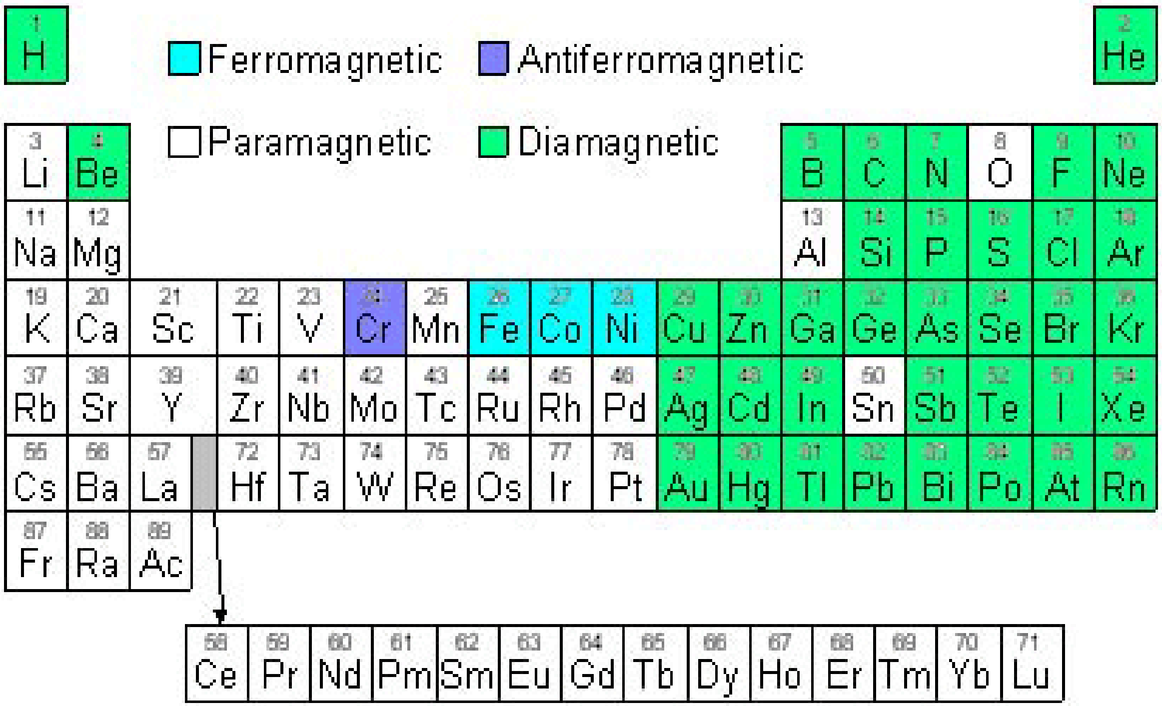
Magnetization (M):
magnetic field induced in sample in external magnetic field (H)

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)**



RoomTemperature MAGNETISM OF PURE ELEMENTS



Ferromagnetism in metals

- Only Fe, Co, Ni RT-FM
- Besides unpaired electrons, "exchange interaction" condition should be fulfilled
- This depends on crystal structure/atomic distances:

  - normal Fe FM, but austenite-type Fe not

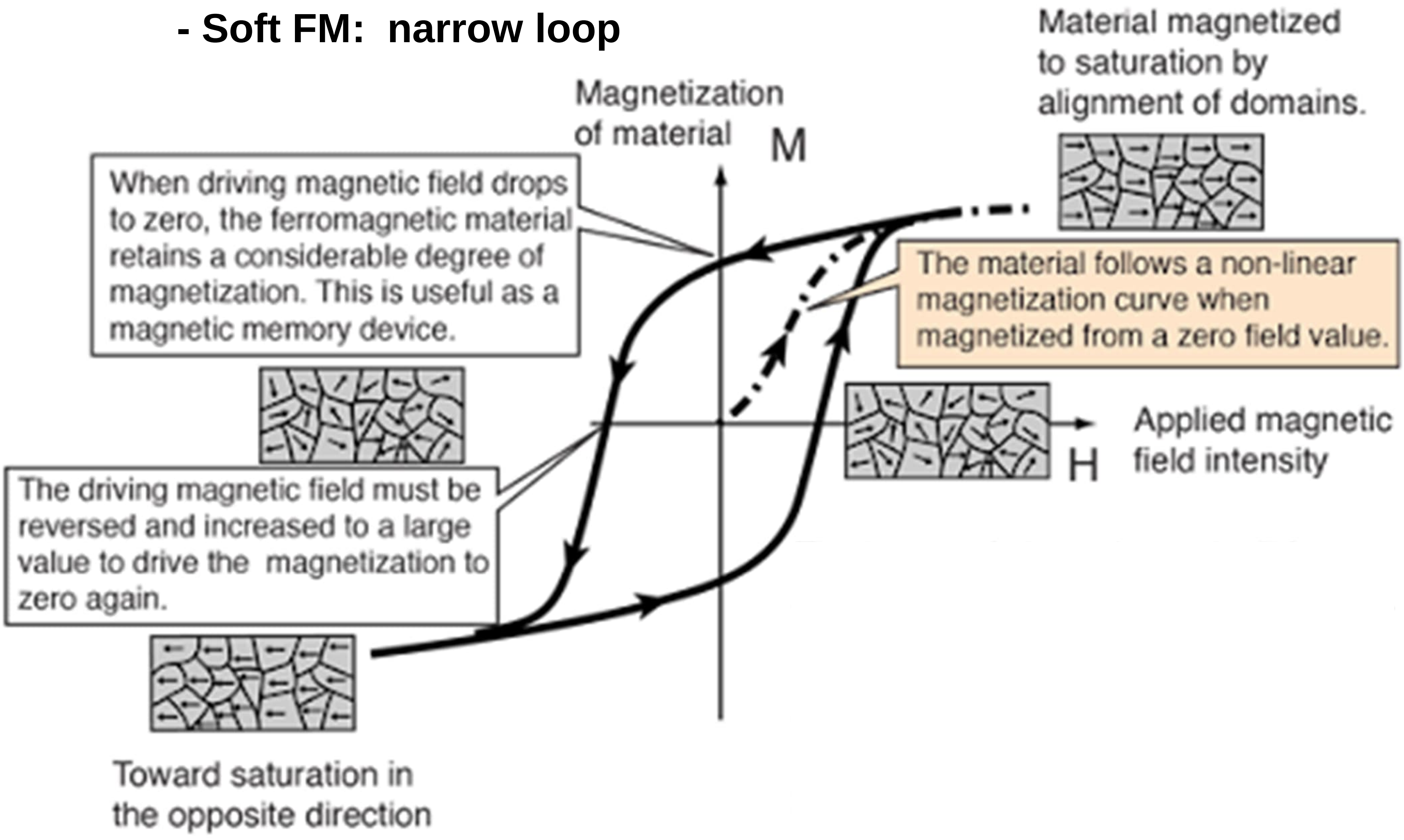
  - pure Mn not FM (too short Mn-Mn distance), but some Mn alloys are (longer Mn-Mn distance)

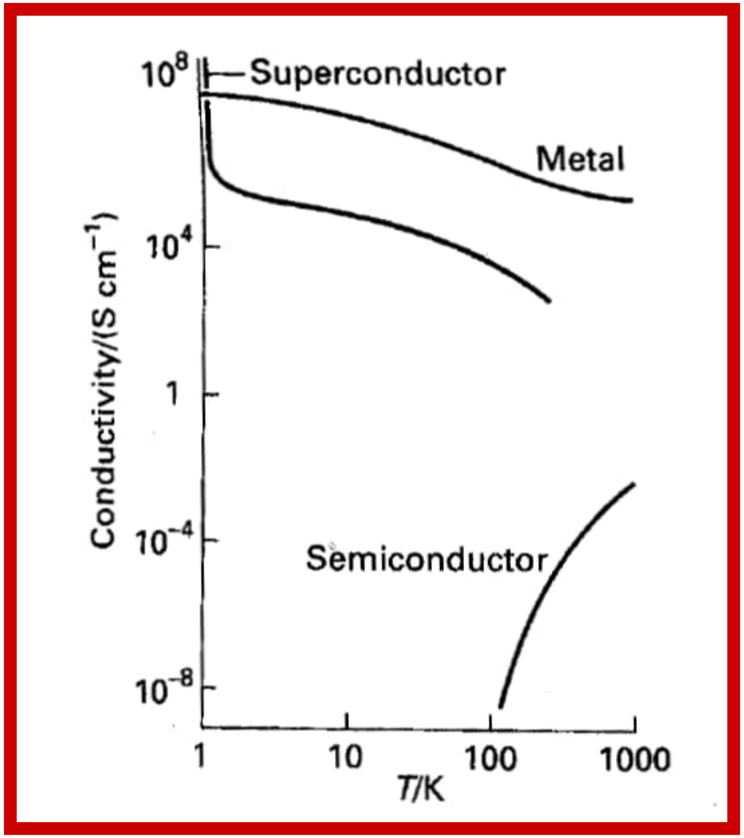
Curie temperatures (in K)

Co	1388
Sm_2Co_{17}	1070
Fe	1043
$SmCo_5$	990
Fe_3O_4	858
$NiFe_2O_4$	858
$CuFe_2O_4$	728
$MgFe_2O_4$	713
MnBi	630
Ni	627
MnSb	587
$Nd_2Fe_{14}B$	580
$MnFe_2O_4$	573
$Y_3Fe_5O_{12}$	560
CrO_2	386
MnAs	318
Gd	292
Dy	88
Er	32
EuO	69

Hystersis Loop of Ferromagnetic Materials

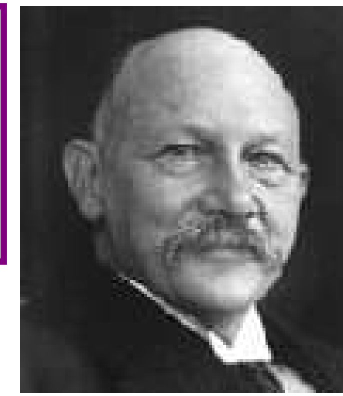
- Coersivity field & Remanent magnetization
- Hard FM: wide loop
- Soft FM: narrow loop



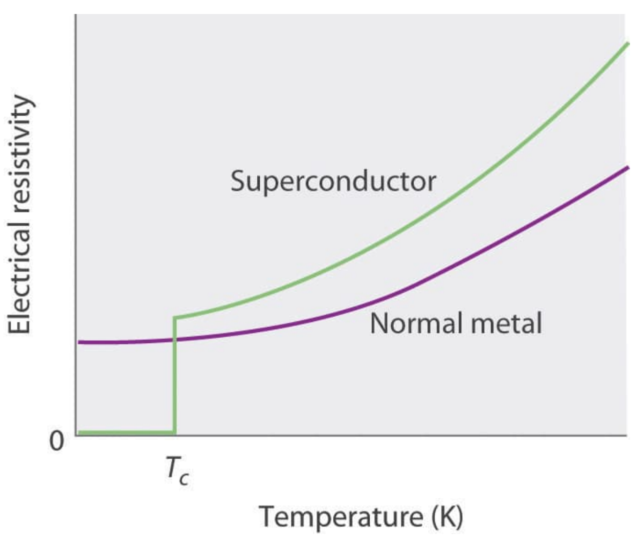


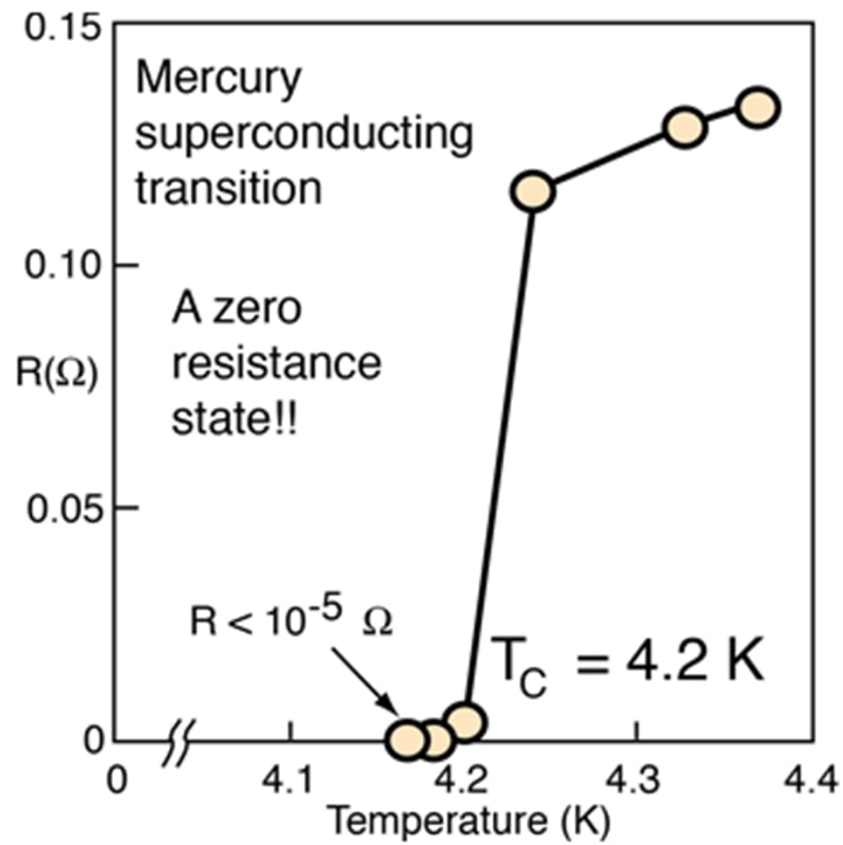
Superconductivity

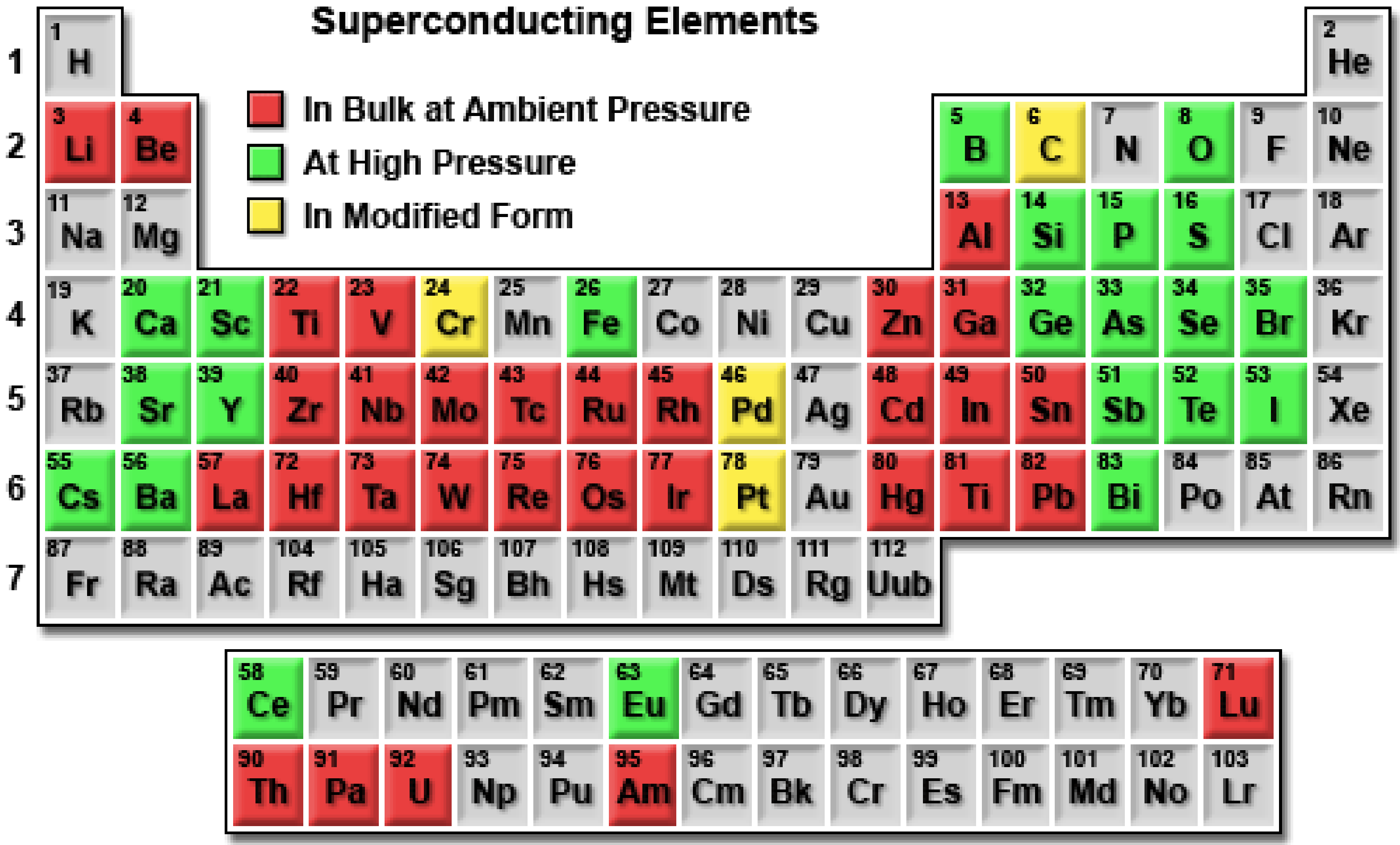
- 1911 Kamerlingh-Onnes
- $\rho = 0$



Nobel 1913

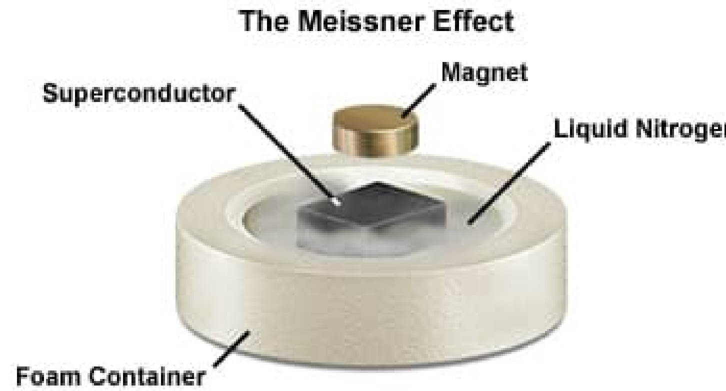





Superconducting Elements
In Bulk at Ambient Pressure
At High Pressure
In Modified Form
1
2
3
4
5
6
7
1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 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 La
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 Rn
87 Fr
88 Ra
89 Ac
104 Rf
105 Ha
106 Sg
107 Bh
108 Hs
109 Mt
110 Ds
111 Rg
112 Uub
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
90 Th
91 Pa
92 U
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cr
99 Es
100 Fm
101 Md
102 No
103 Lr

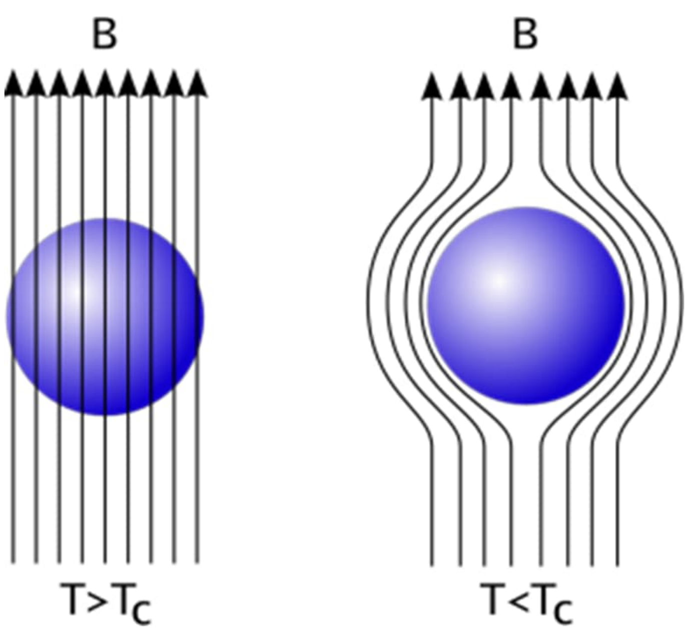
”Meissner effect”

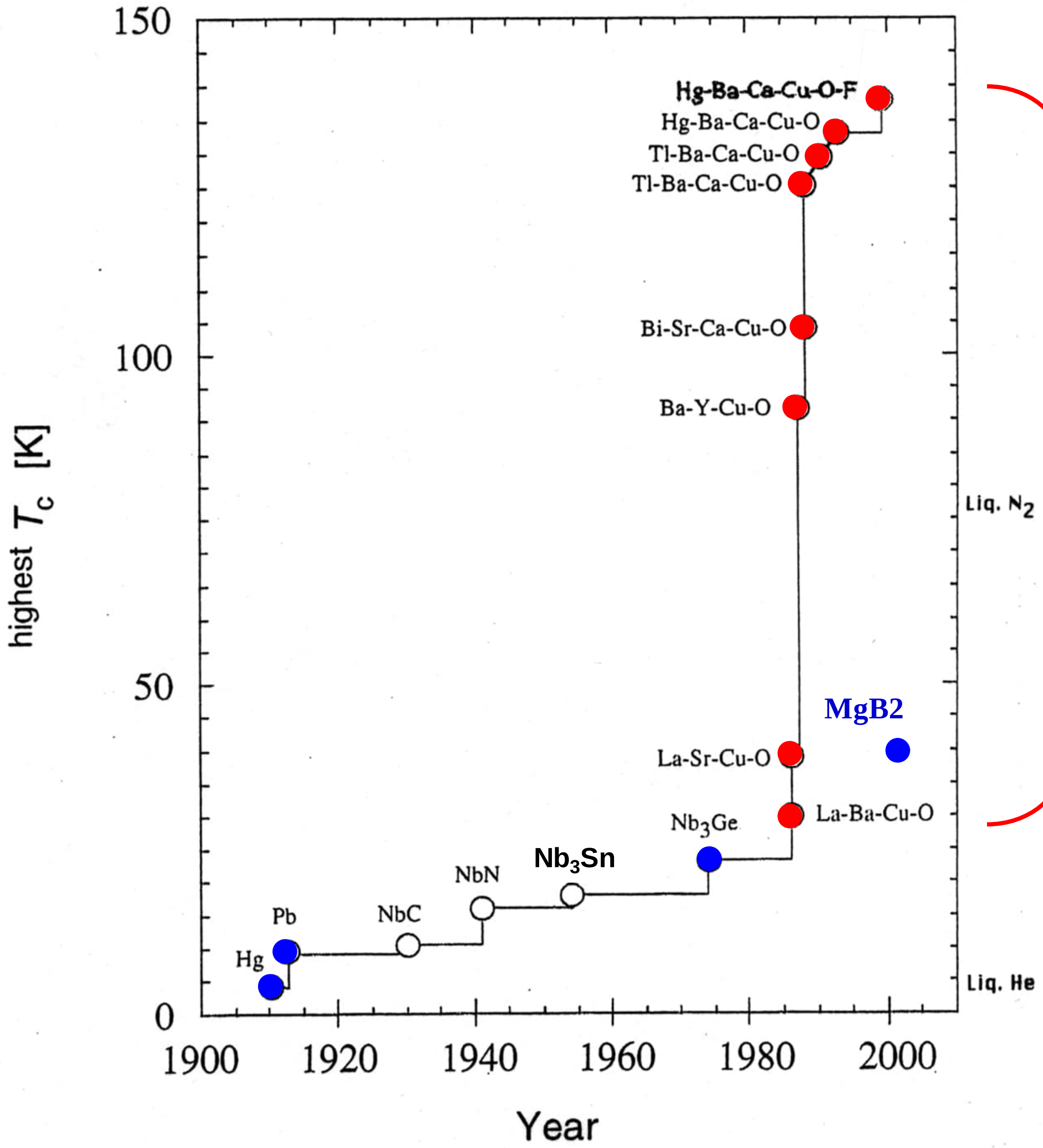
1933 Meissner and Ochenfeld:
$\chi = B/H < 0 \rightarrow$ levitation

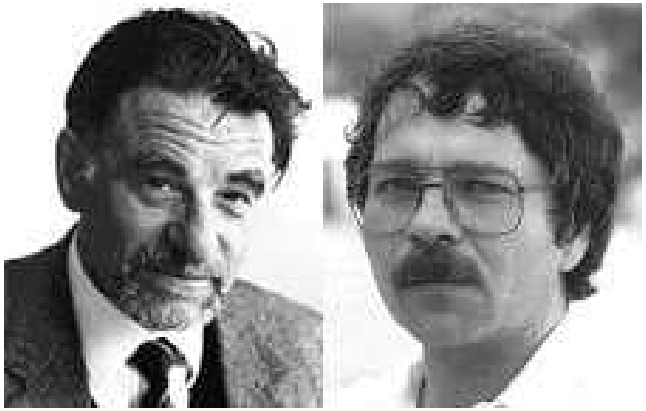


Super-Maglev Train

- **603 km / hour**
- **Test line 42.8 km**





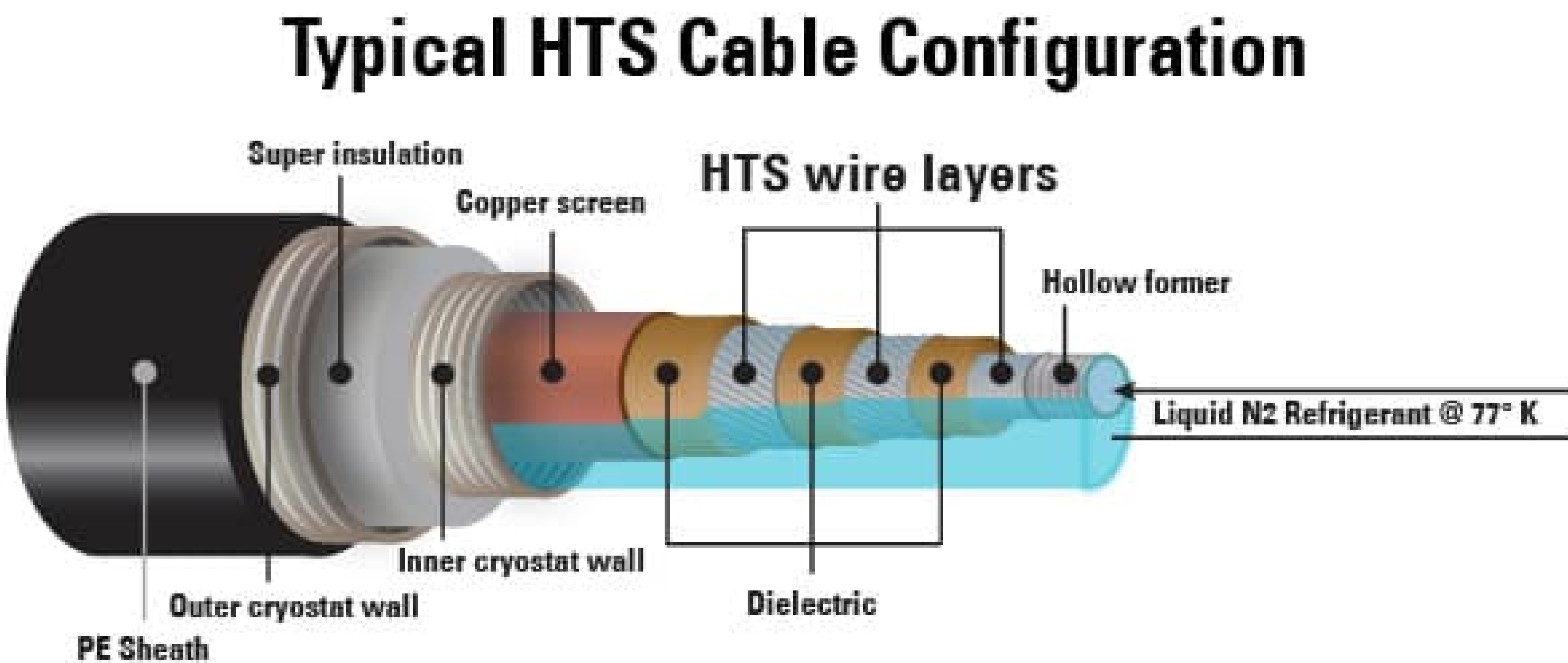


High-*Tc* superconductivity

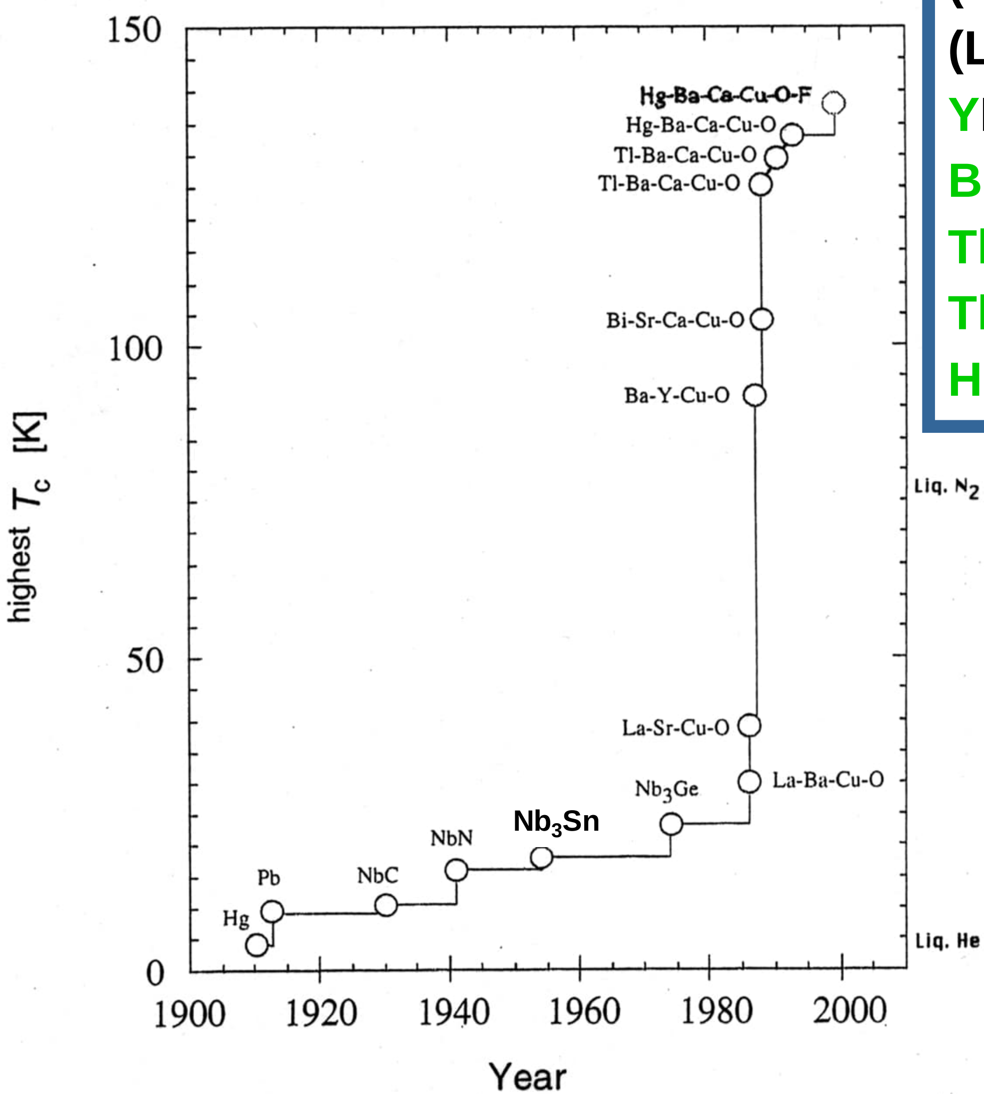
- 1986: Bednorz and Müller
- $(La,Ba)_2CuO_4$ T_c = ~30 K
- Nobel 1987

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)



Search for new high-*Tc* superconductors



$(La_{0.92}Ba_{0.08})CuO_4$

$(La_{0.92}Sr_{0.08})_2CuO_4$

$YBa_2Cu_3O_7$

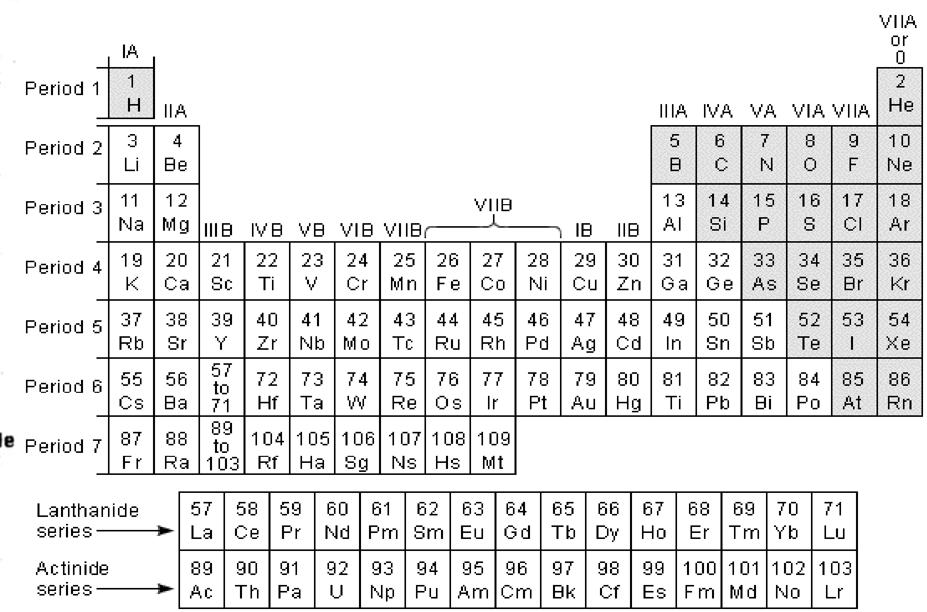
$Bi_2Sr_2Ca_2Cu_3O_{10}$

$Tl_2Ba_2Ca_2Cu_3O_{10}$

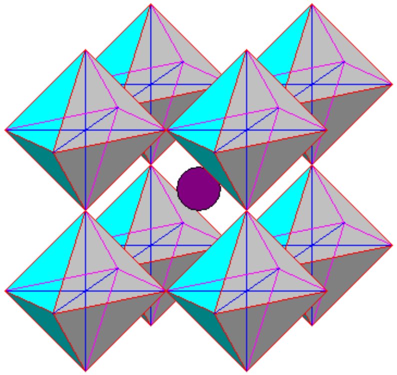
$TlBa_2Ca_2Cu_3O_9$

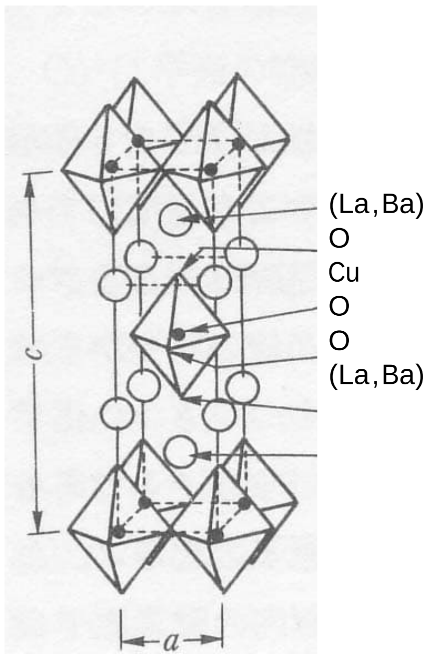
$HgBa_2Ca_2Cu_3O_9$

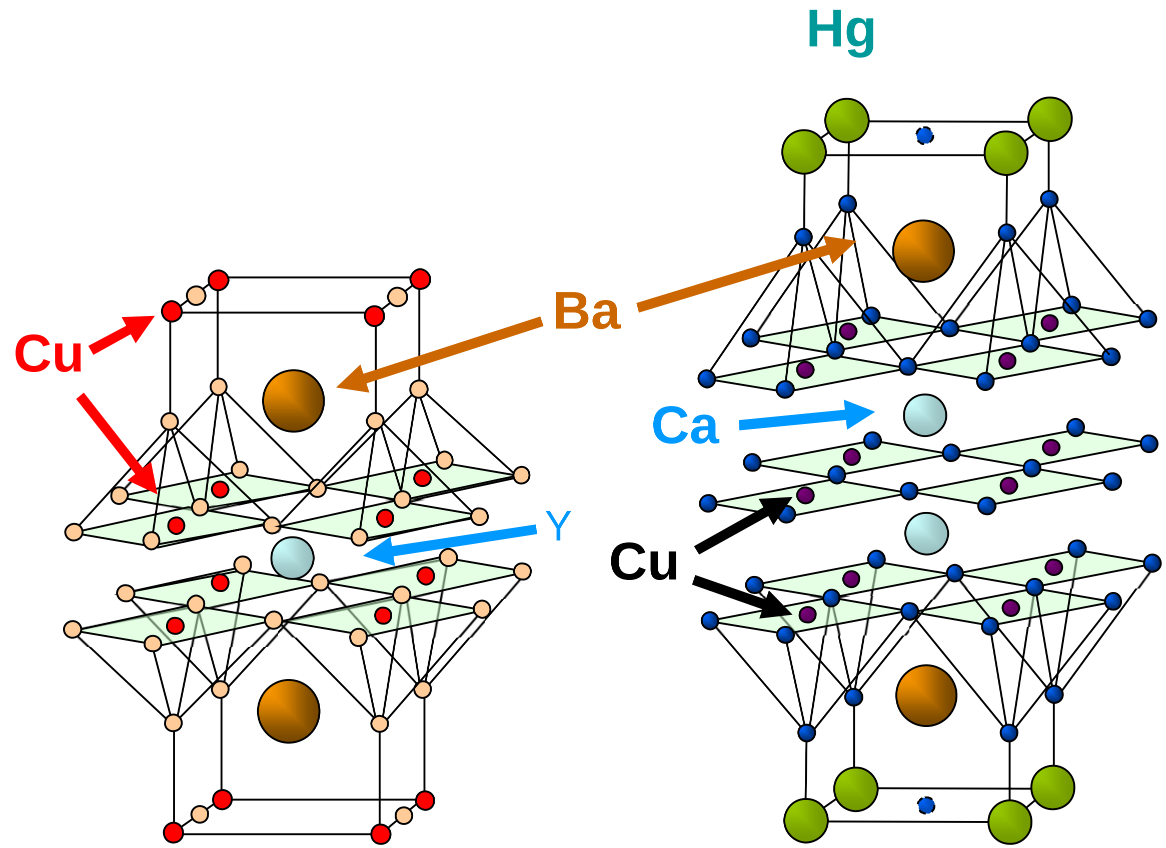
- **Chemical pressure**
- **No. of CuO_2 planes**
- **Inert-pair effect**



Crystal Structures of High-T_c Superconductive Copper Oxides







$(La,Ba)_2CuO_{4+\delta}$

$T_c \approx 35$ K

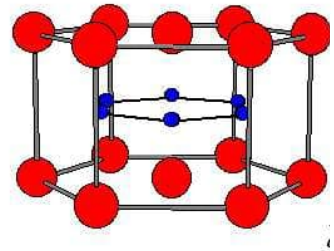
$YBa_2Cu_3O_{7-\delta}$

$T_c \approx 92$ K

$HgBa_2Ca_2Cu_3O_{9-\delta}$

$T_c \approx 135$ K

Akimitsu 2001: MgB_2



Hosono 2006 → [La(O,F)][FeAs]