TENTATIVE LECTURE SCHEDULE

		Date	Topic
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 Complex & POM, MOF, MLD
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Pt metals & Magnetism
12.	Wed	13.10.	Co, Cu & Superconductivity
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 (in ZOOM)

PRESENTATION TOPICS/SCHEDULE

Wed	06.10.	Nb:	Toivonen
Fri	08.10.	Mo:	Ahmed, Shamshad
Mon	11.10.	Mn:	Majaniemi, Thakur, Ahkiola
		Ru:	Ichanson, Locqueville, Olsio
Wed	13.10.	Co:	Ekholm, Olander, Syväniemi
		Cu:	Kolawole, Nguyen, Munib
Fri	15.10.	In:	Kovanen, Ogunyemi, Svinhufvud
		Te:	Huhtakangas, Wallin, Kaarne
Mon	18.10.	Eu:	Sonphasit, Tuisku
		Nd:	Jussila, Siuro, Perttu
		U:	Sinkkonen, Wennberg, Partanen

QUESTIONS: Lecture 12

1. In which condition (acidic or basic) Cu^{+} tends to disproportionate ?

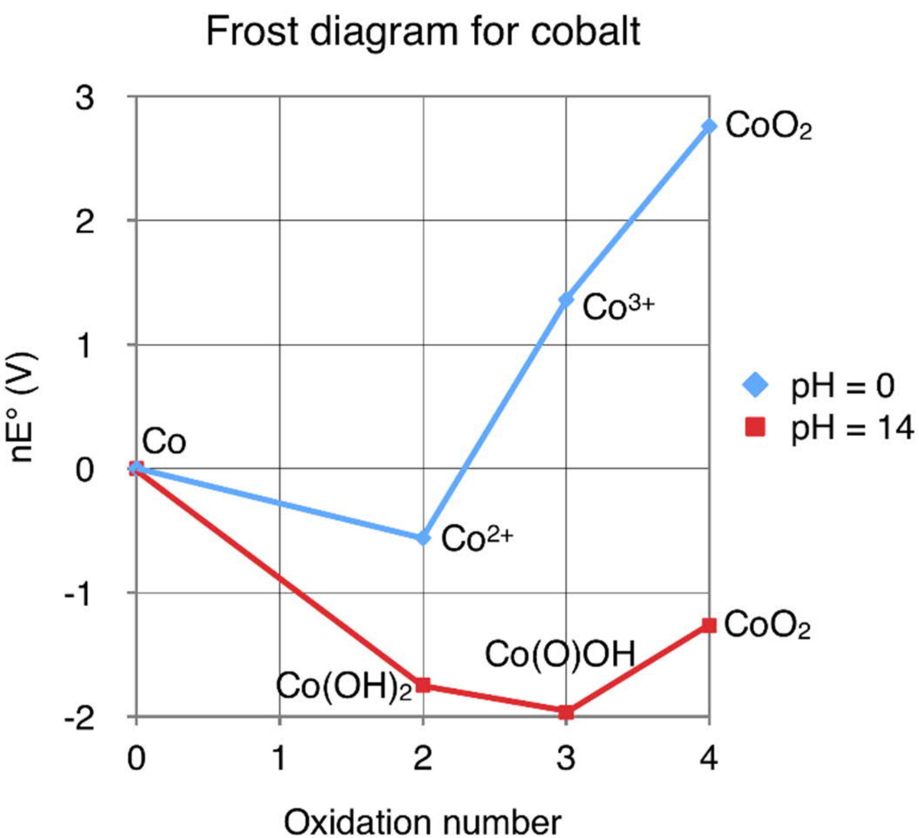
2. Which one(s) of the followings are superconducting: Hg, Cu, $La_2CuO_{4.0}$, $La_2CuO_{4.1}$, $(La_{0.9}Ba_{0.1})_2CuO_{4.0}$ and $HgBa_2Ca_2Cu_3O_{8.0}$? Justify your choices.

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	

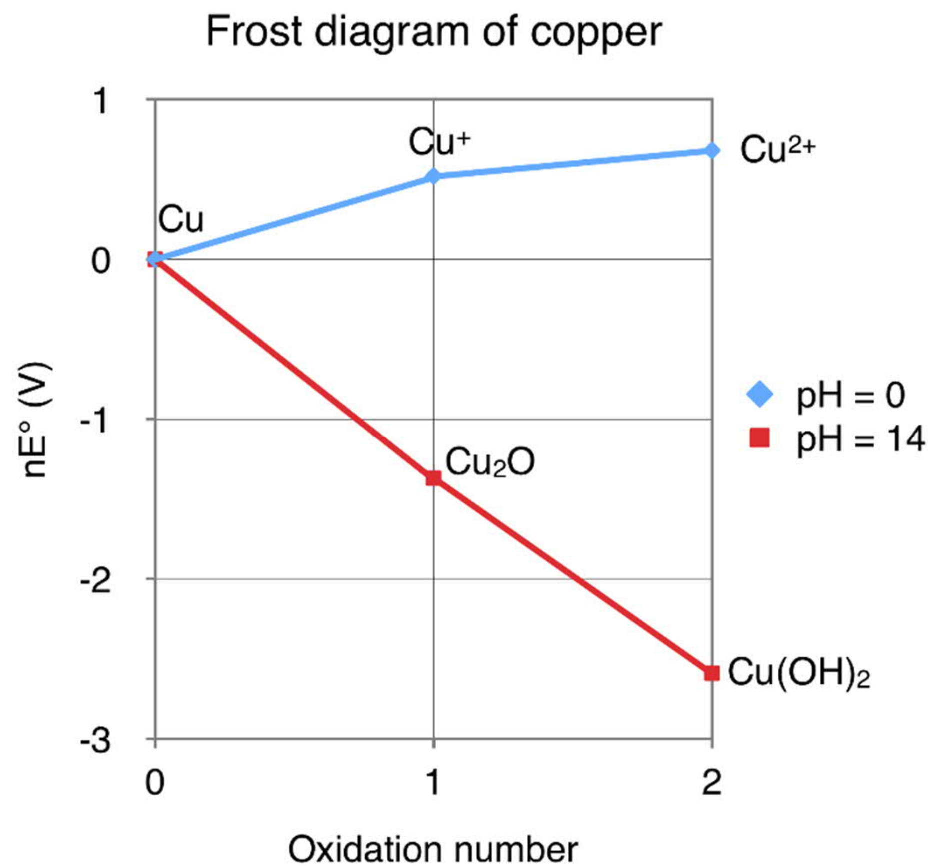
Element	Symbol	Electronic Configuration
Scandium	Sc	$[Ar]3d^14s^2$
Titanium	Ti	$[Ar]3d^24s^2$
Vanadium	V	$[Ar]3d^34s^2$
Chromium	Cr	$[Ar]3d^54s^1$
Manganese	Mn	$[Ar]3d^54s^2$
Iron	Fe	$[Ar]3d^64s^2$
Cobalt	Co	$[Ar]3d^74s^2$
Nickel	Ni	$[Ar]3d^84s^2$
Copper	Cu	$[Ar]3d^{10}4s^1$
Zinc	Zn	$[Ar]3d^{10}4s^2$

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



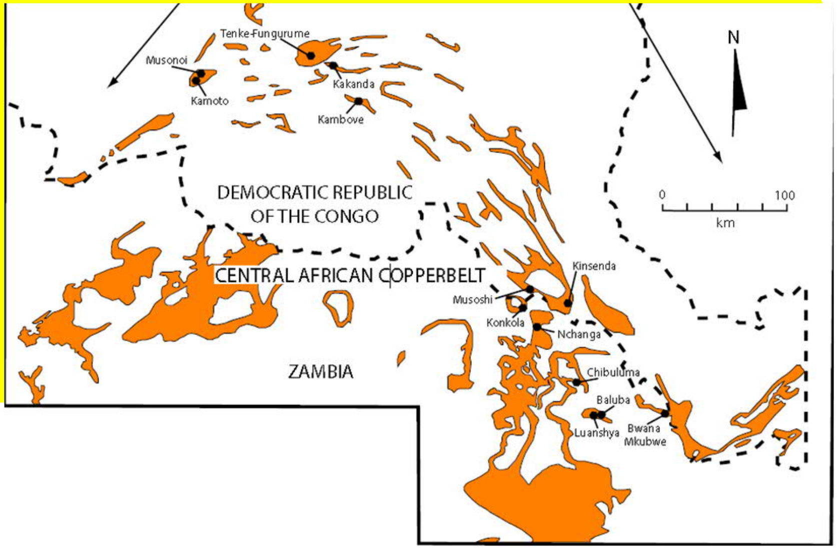
Frost diagram for cobalt
3
2
1
0
-1
-2
nE° (V)
0
1
2
3
4
Oxidation number
Co
Co2+
Co3+
CoO2
Co(OH)2
Co(O)OH
CoO2
pH = 0
pH = 14



Frost diagram of copper
1
0
-1
-2
-3
nE° (V)
0
1
2
Oxidation number
Cu
Cu+
Cu2+
Cu2O
Cu(OH)2
pH = 0
pH = 14

COBALT

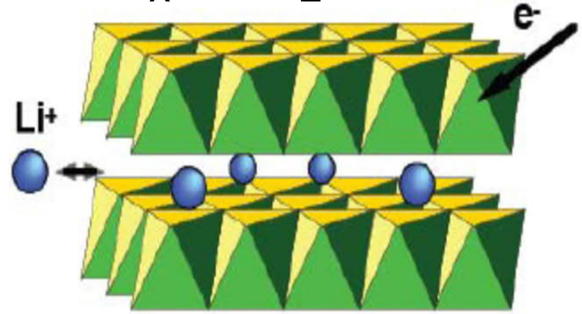
- Cobalt-based blue pigments (cobalt blue; $CoAl_2O_4$) have been used since ancient times in jewelry, paints and glass
- Ancient miners used the German name *kobold ore* (*goblin ore*) for some blue-pigment producing minerals
- In 1735 metallic cobalt was reduced from these ores (first metal discovered 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 → $LiCoO_2$!
- OXIDES:
  - CoO: green, rock-salt, AFM (T_N = 291 K)
  - Co_3O_4: blue, spinel, AFM (T_N = 40 K)
  - Co_2O_3: black



Freeport Cobalt

In Kokkola:
Outokumpu → OMG → FreeportCobalt → Umicore

Li_xCoO_2



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

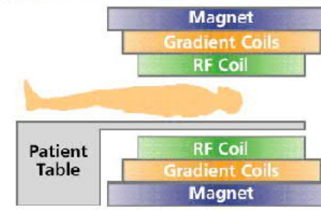
Superconducting Magnets

- 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

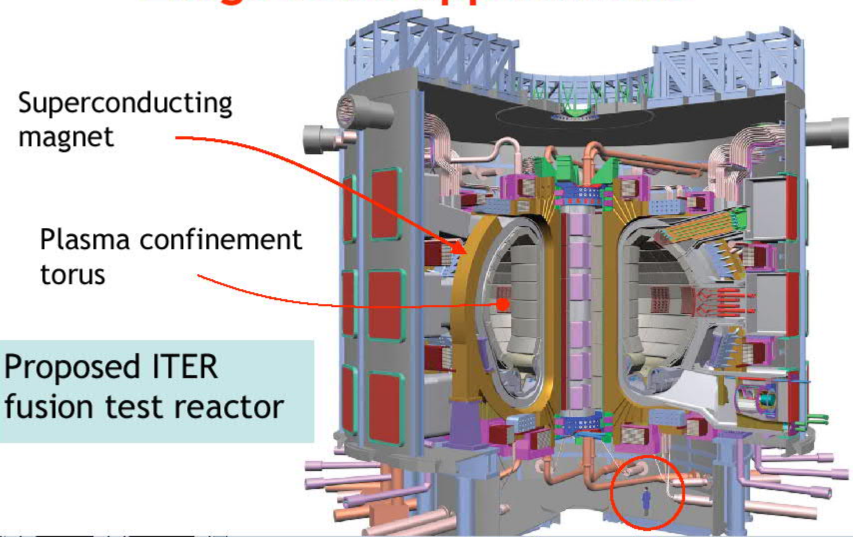
- Magnetic Resonance Imaging typically done at 1.5 T
- Superconducting magnet to provides static magnetic field
- Spatial resolution of positions of tracer atomic nuclei.



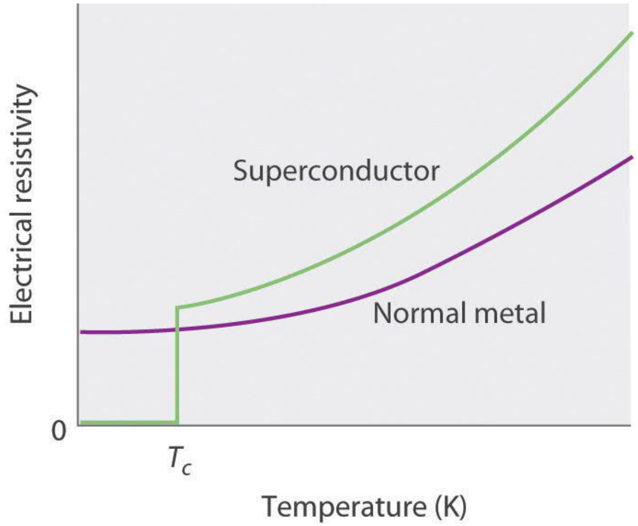
900 MHz NMR (UW Chemistry)

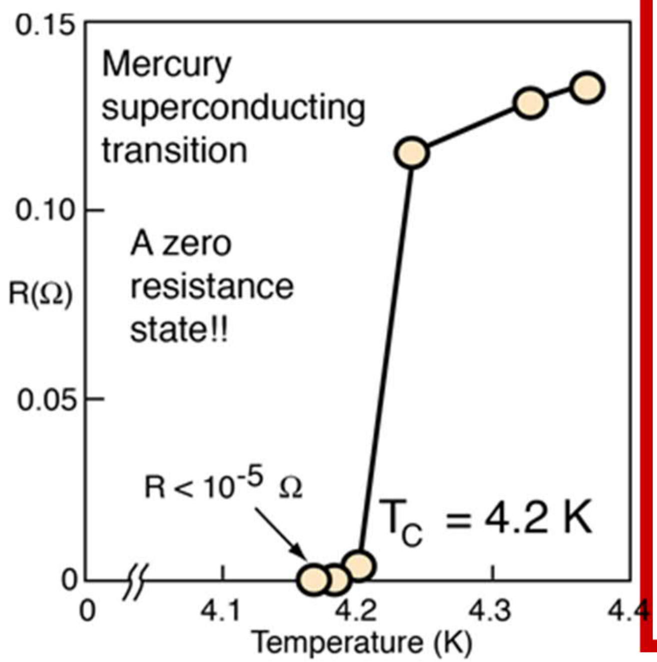
21.7 T field

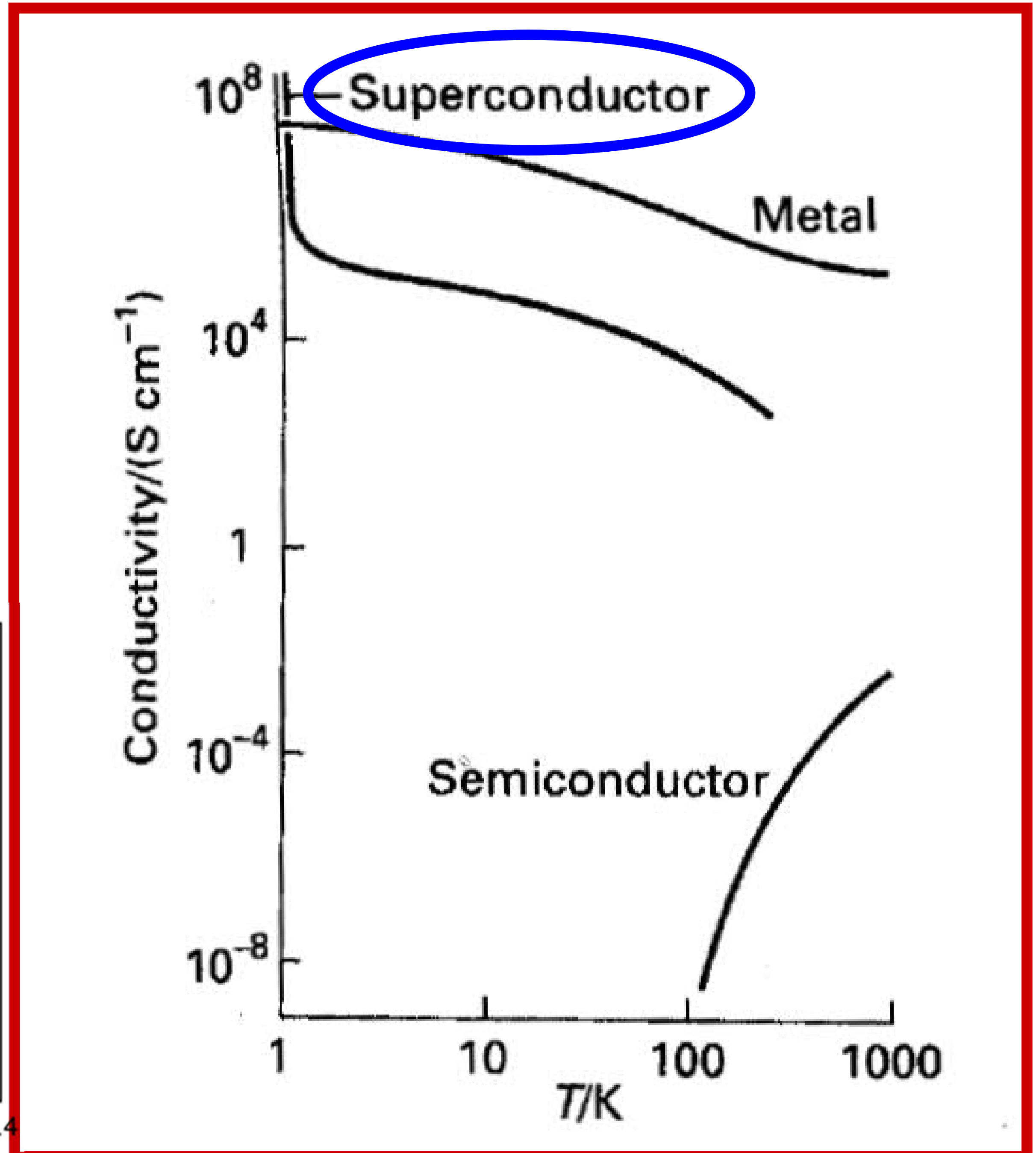
Large scale applications



Proposed ITER fusion test reactor


Electrical resistivity
Superconductor
Normal metal
0
T_c
Temperature (K)


0.15
0.10
0.05
0
R(Ω)
Mercury superconducting transition
A zero resistance state!!
R < 10^-5 Ω
T_C = 4.2 K
0
4.1
4.2
4.3
4.4
Temperature (K)


Superconductor
Metal
Semiconductor
10^8
10^4
1
10^{-4}
10^{-8}
Conductivity/(S cm^{-1})
1
10
100
1000
T/K

SUPERCONDUCTIVITY

Nobel 1913

Superconductivity

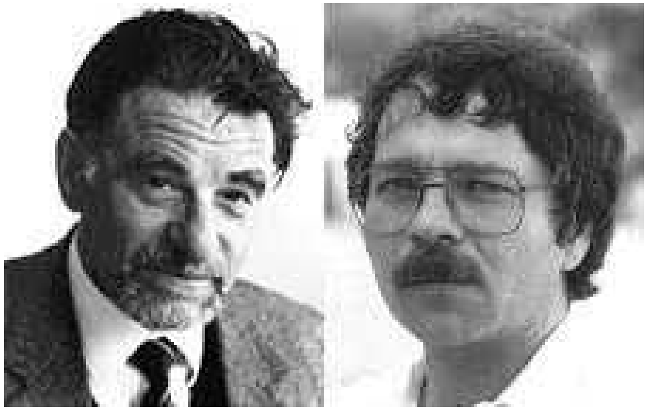
1911 Kamerlingh-Onnes: $\rho = 0$
- Hg with $Tc = 4.2$ K

"Meissner effect"

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

High-*Tc* superconductivity

1986: Bednorz and Müller
- $(La,Ba)_2CuO_4$ with $T_c = 30 \sim 40$ K



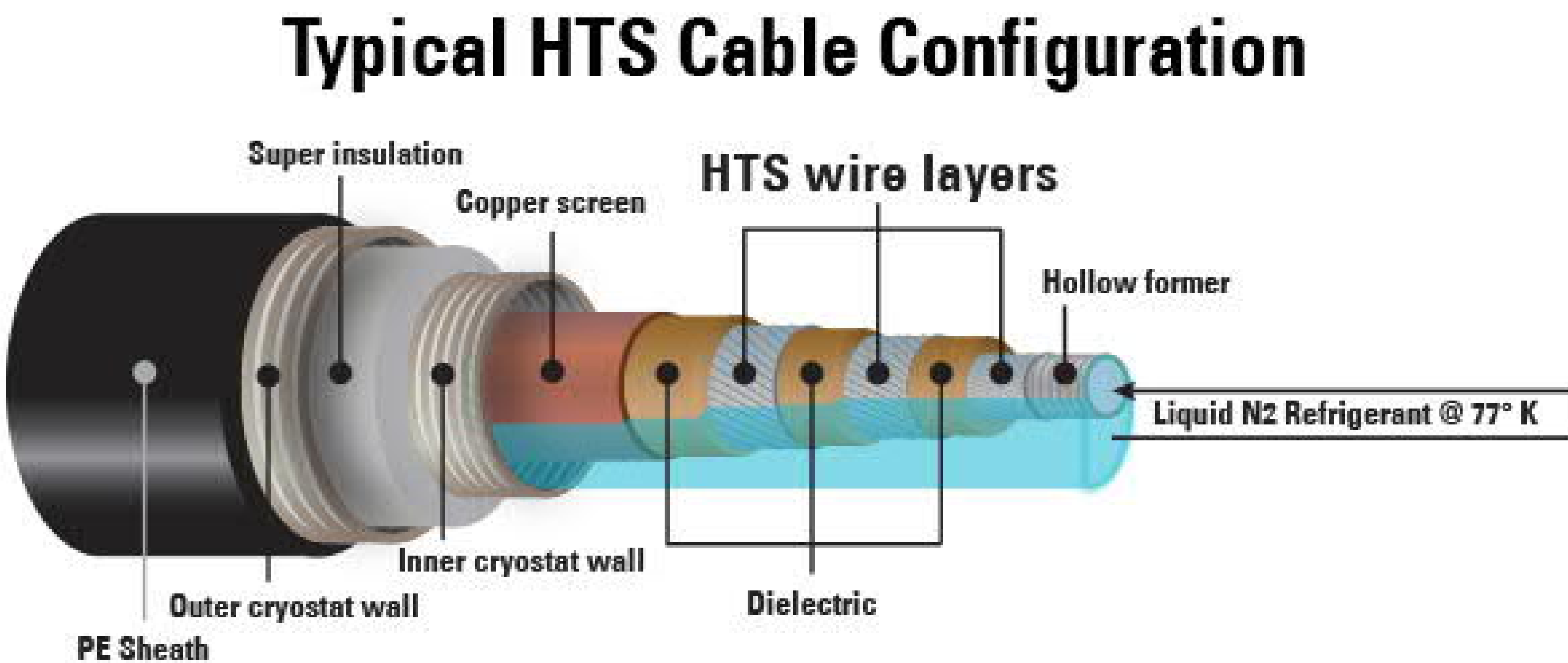
Nobel 1987

Present record in T_c:

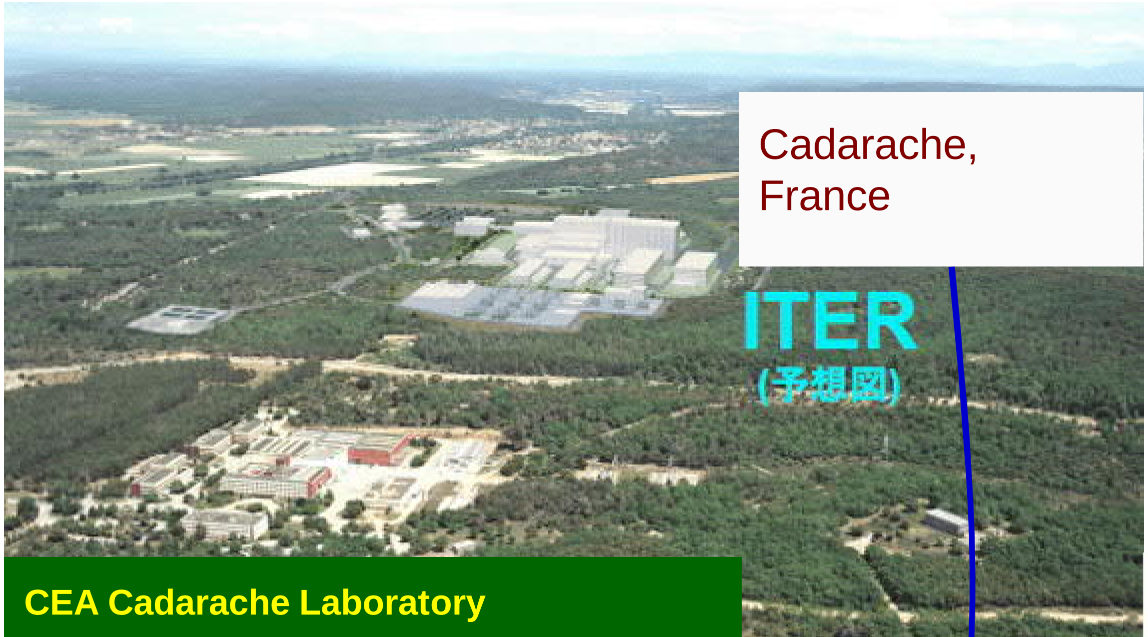
138 K for $HgBa_2Ca_2Cu_3O_{8+\delta}$

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)

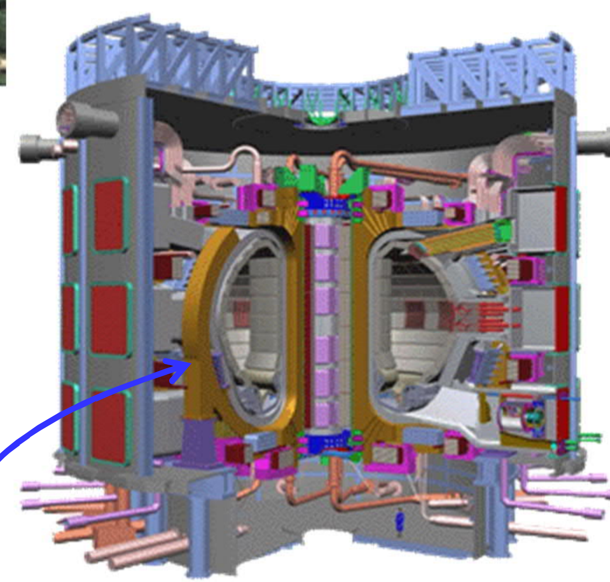


ITER: International Thermonuclear Experimental Reactor

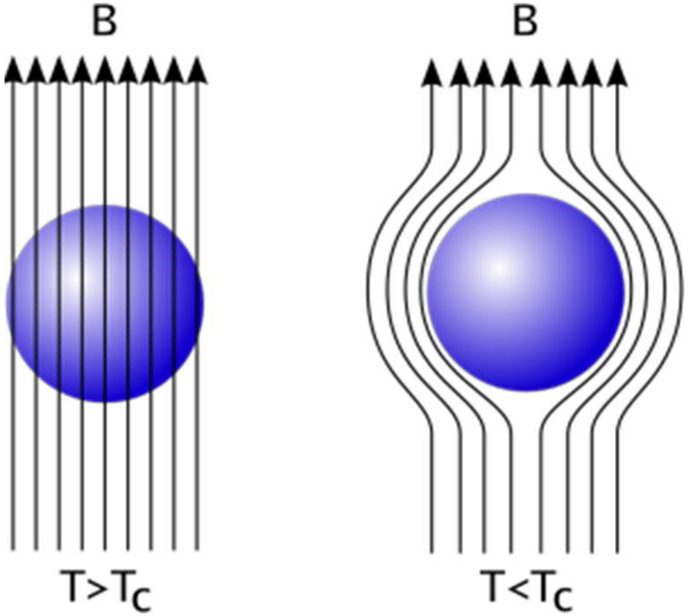


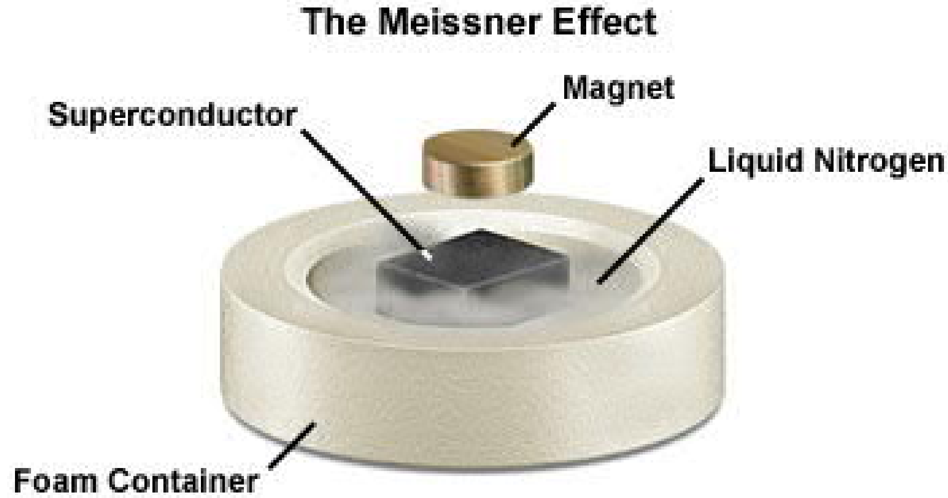
since October, 2007

Nuclear Fusion Reactor



Superconducting Magnets

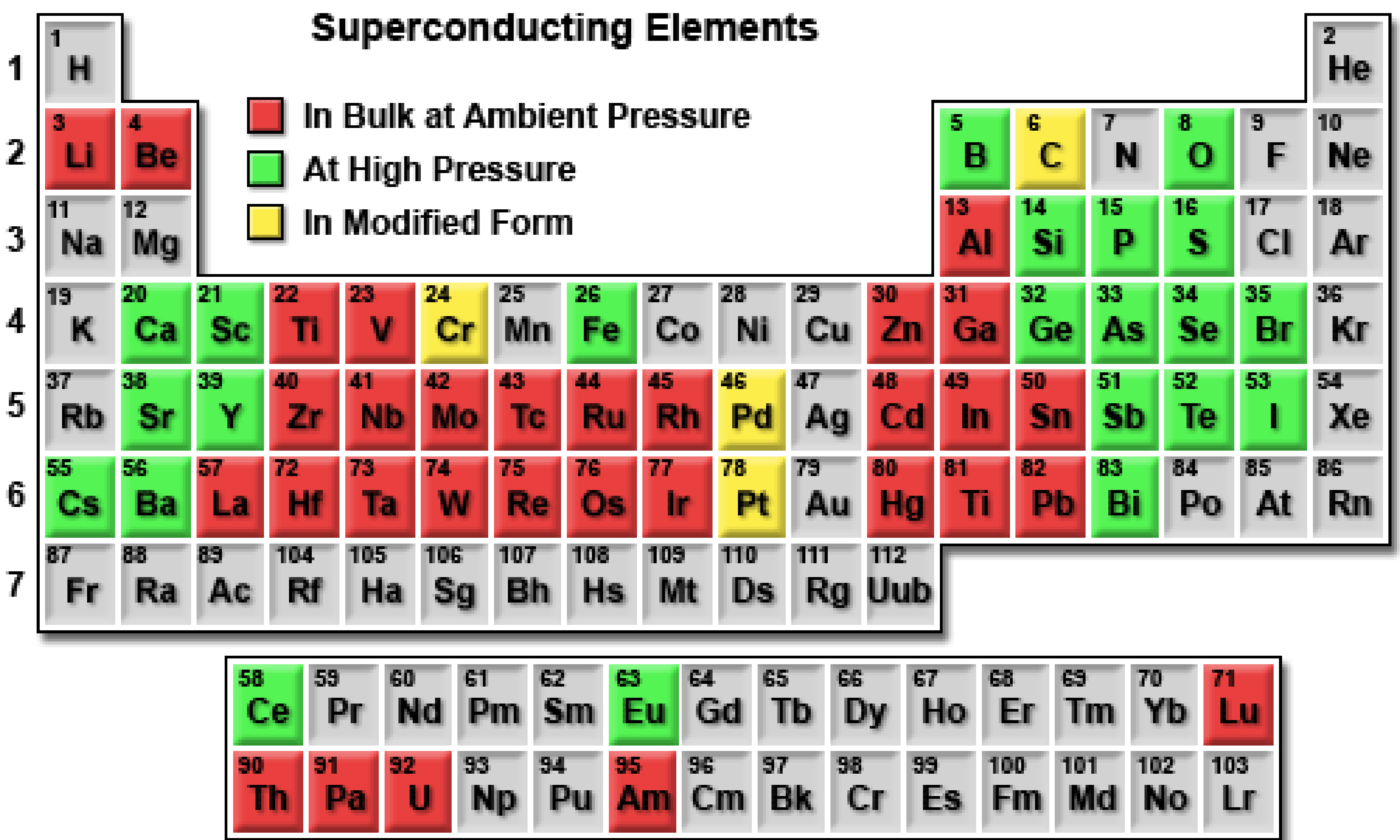

B
B
T>T_C
T<T_C

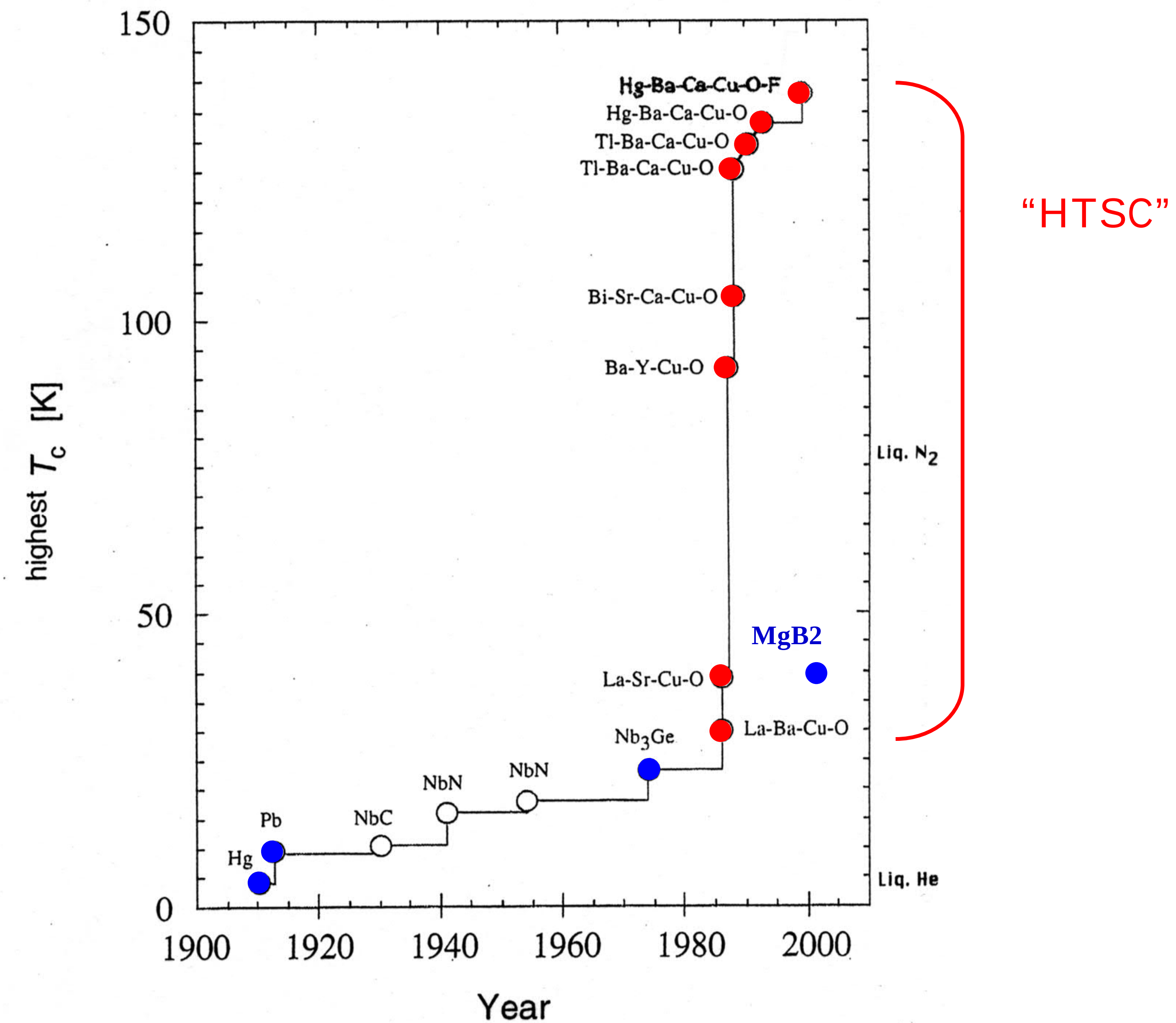

The Meissner Effect
Magnet
Superconductor
Liquid Nitrogen
Foam Container


登録商標
天賞
宮城優良清酒

Super-Maglev Train

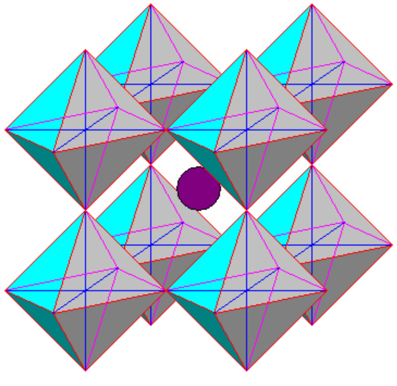
- 603 km / hour
- Test line 42.8 km

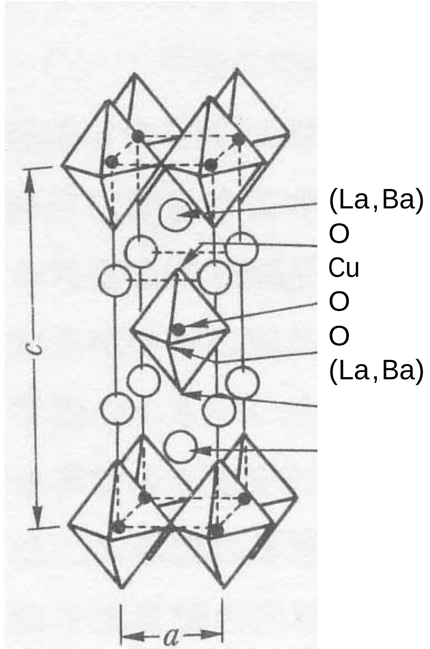

Superconducting Elements
In Bulk at Ambient Pressure
At High Pressure
In Modified Form
1
1 H
2 He
2
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
3
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
4
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
5
37 Rb
38 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 Ti
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
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

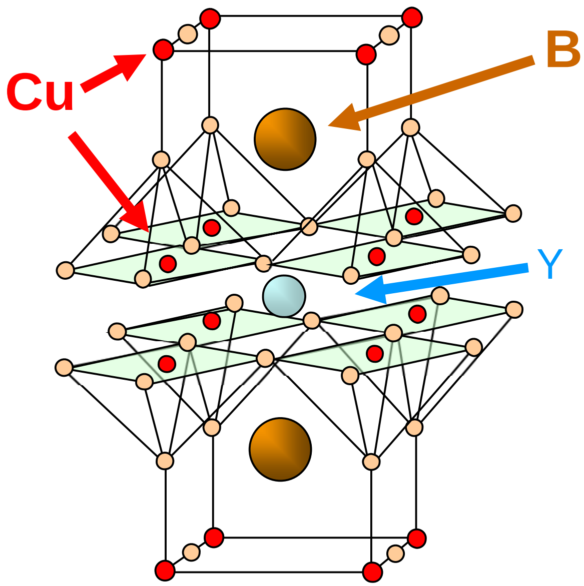


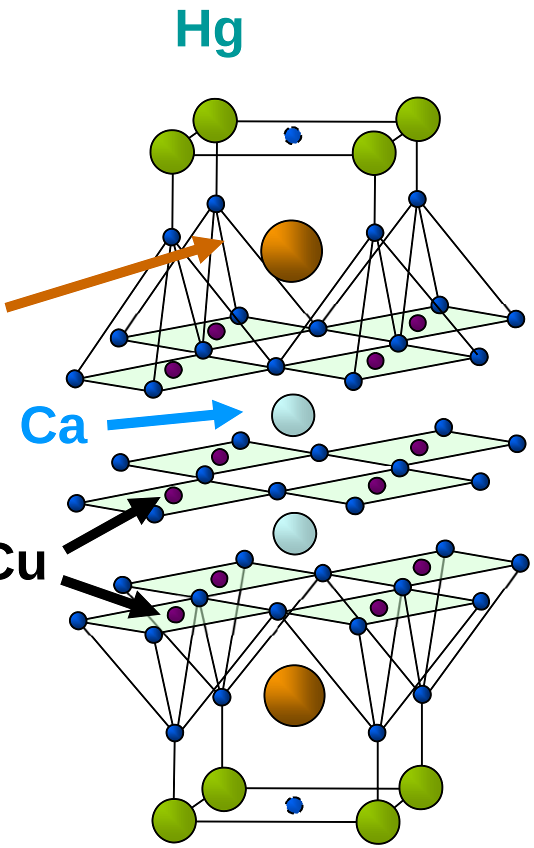
150
100
50
0
highest T_c [K]
1900
1920
1940
1960
1980
2000
Year
Hg
Pb
NbC
NbN
NbN
Nb_3Ge
La-Ba-Cu-O
La-Sr-Cu-O
Ba-Y-Cu-O
Bi-Sr-Ca-Cu-O
Tl-Ba-Ca-Cu-O
Tl-Ba-Ca-Cu-O
Hg-Ba-Ca-Cu-O
Hg-Ba-Ca-Cu-O-F
MgB2
Liq. N_2
Liq. He
"HTSC"

Crystal Structures of High-T_c Superconductive Copper Oxides









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

$T_c \approx 35$ K

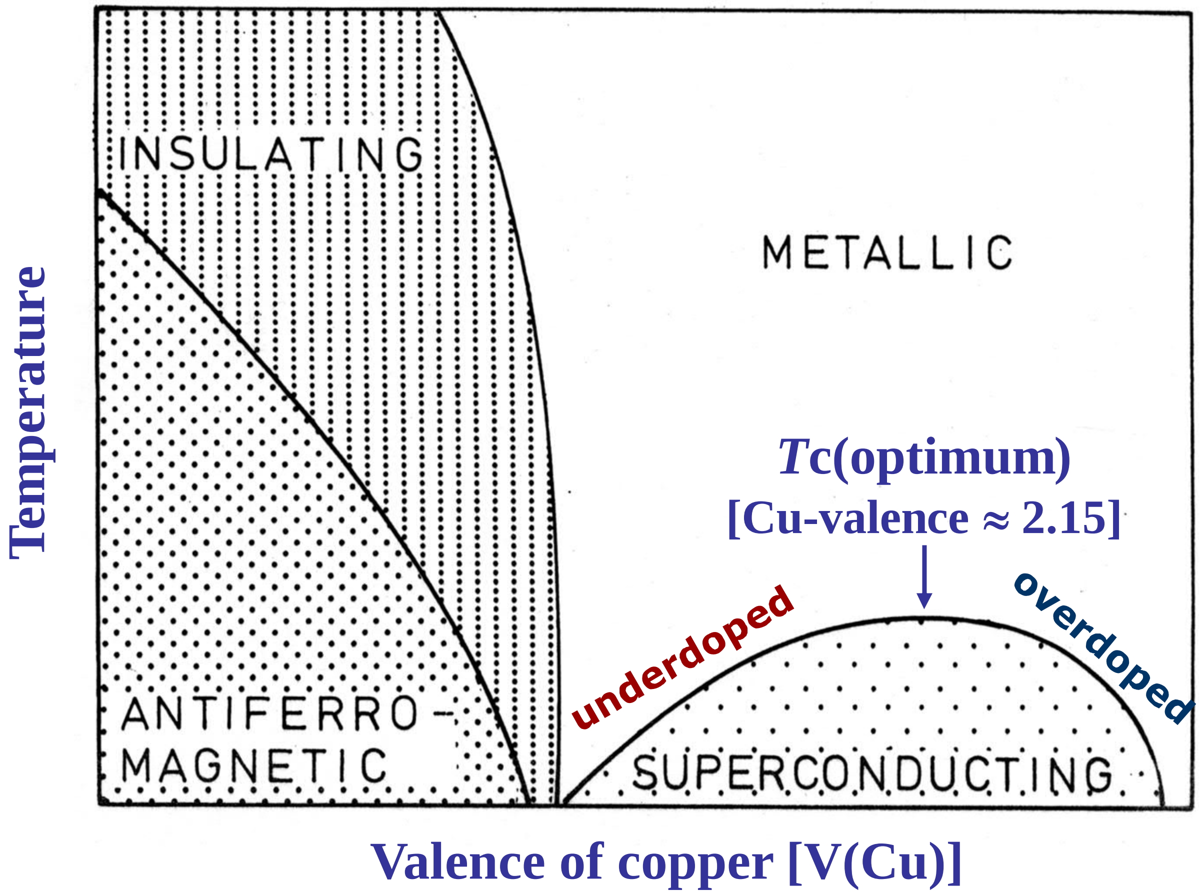
$YBa_2Cu_3O_{7-\delta}$

$T_c \approx 92$ K

$HgBa_2Ca_2Cu_3O_{9-\delta}$

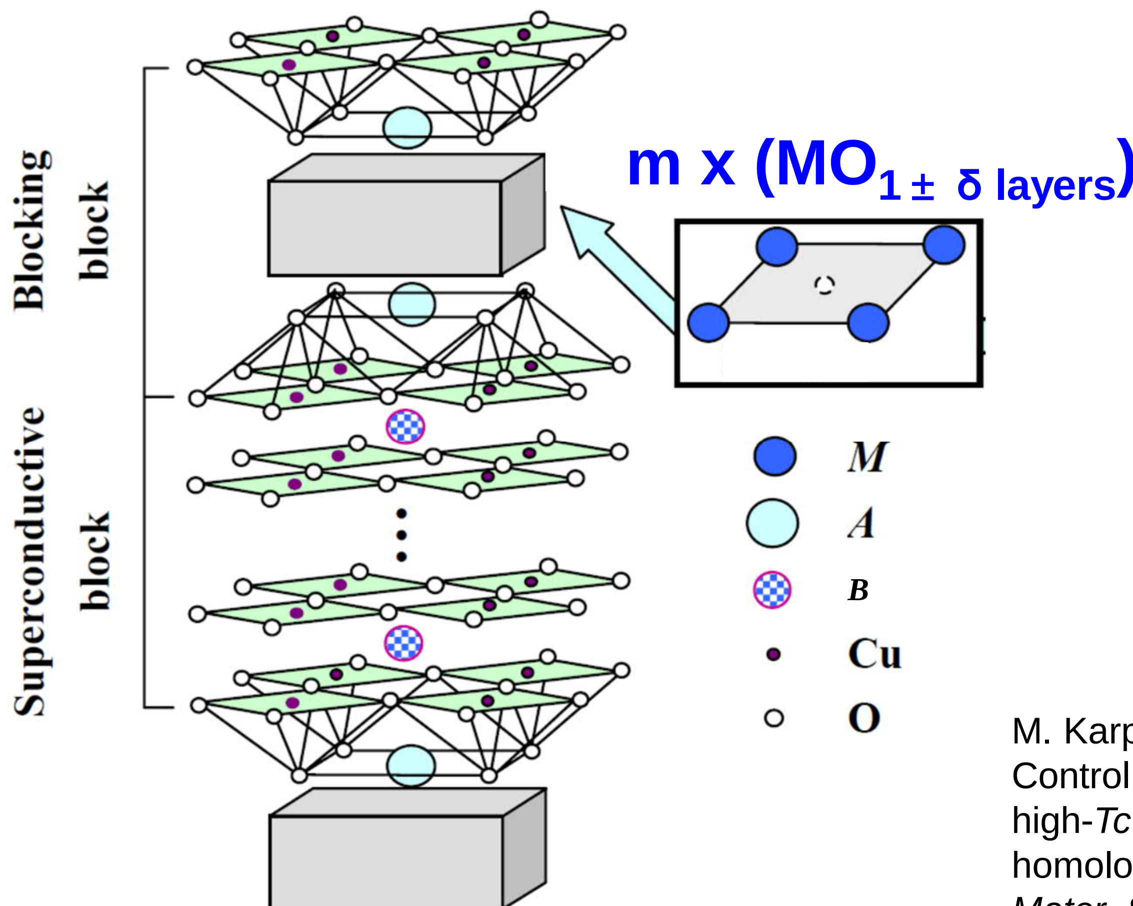
$T_c \approx 135$ K

Phase Diagram of HTSC

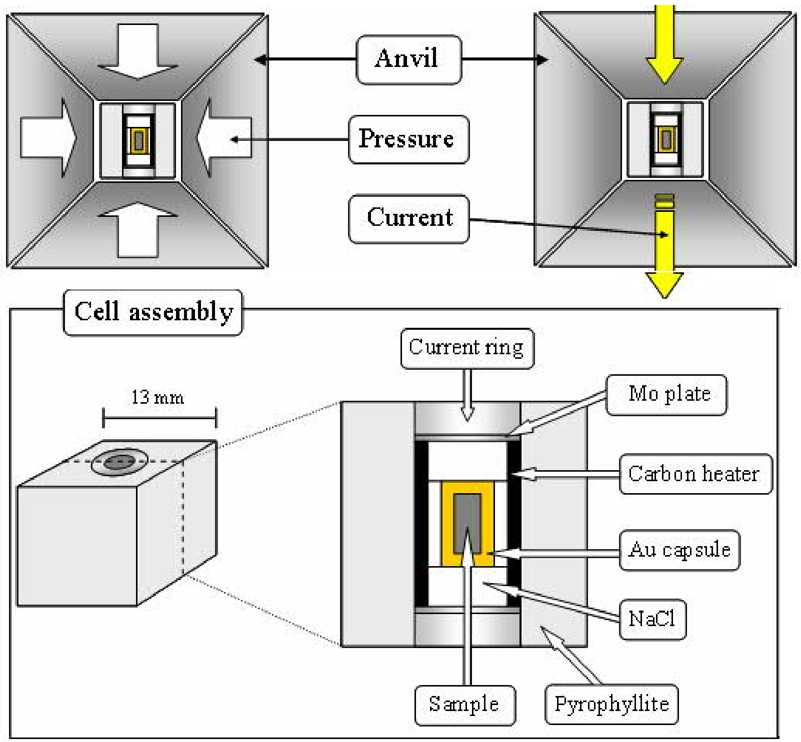


GENERAL FORMULA

- $M_mA_2B_{n-1}Cu_nO_{m+2+2n\pm\delta}$
- **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-*Tc* superconducting properties in homologous series of multi-layered copper oxides,
Mater. Sci. Eng. R **26**, 51-96 (1999).



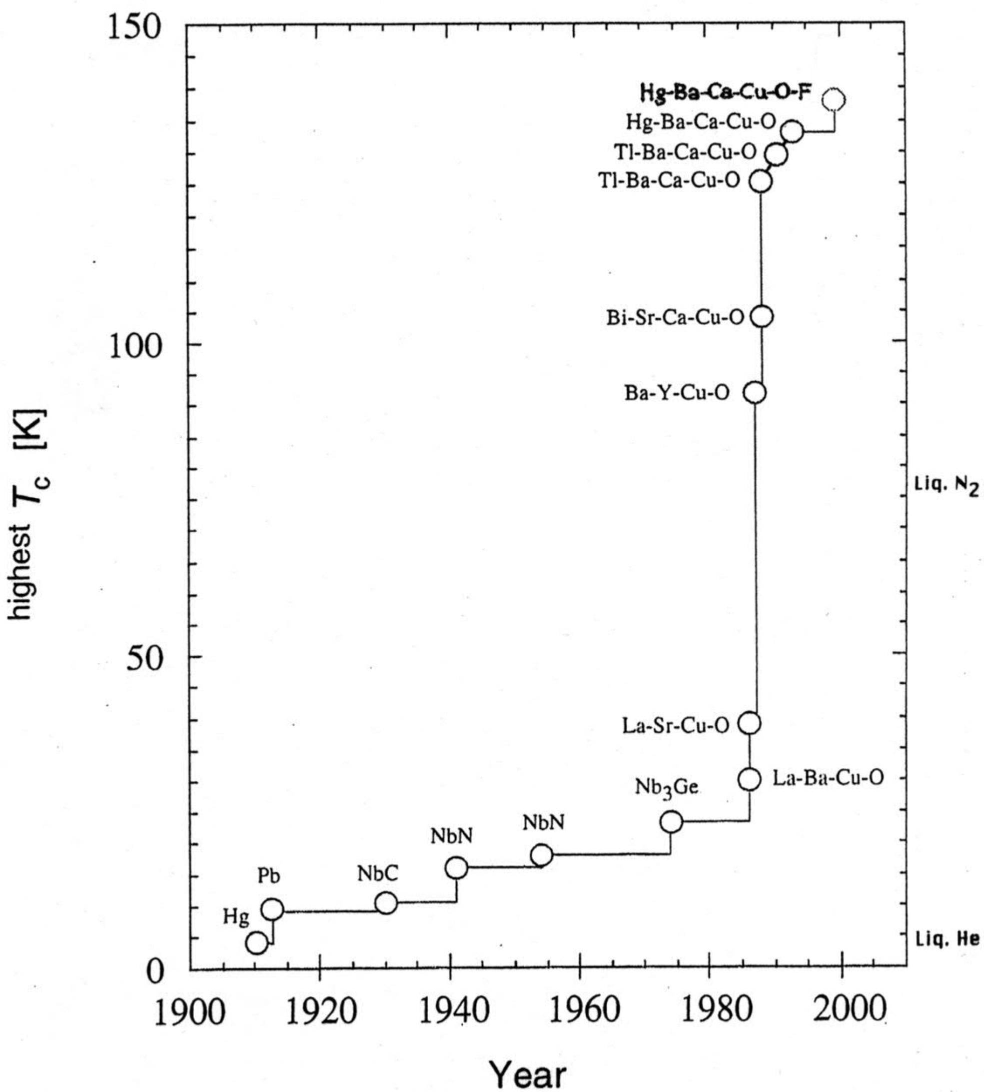
HIGH-PRESSURE SYNTHESIS

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

HP equipment
at Tokyo Tech

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

Search for new high-*Tc* superconductors



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

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

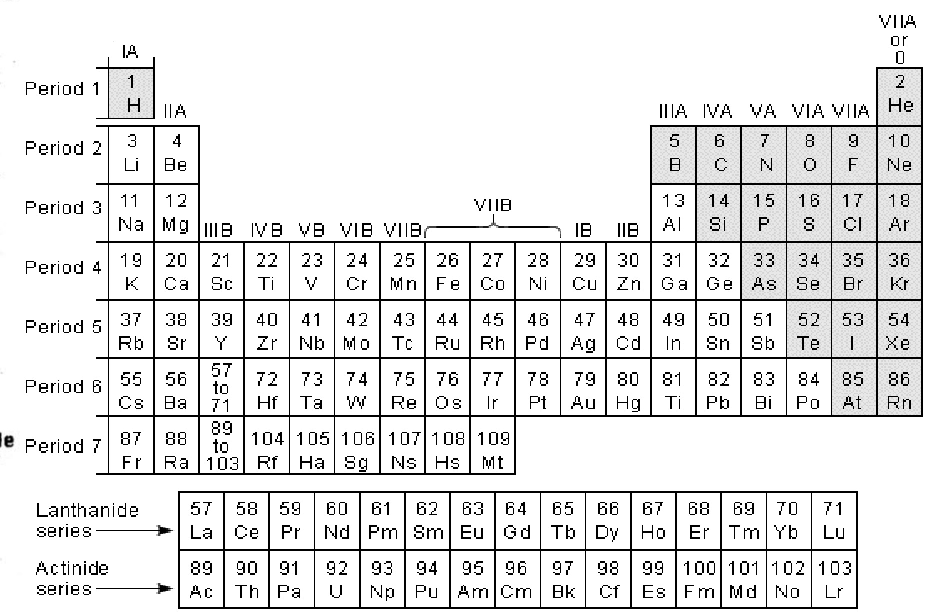
$YBa_2Cu_3O_7$

$Bi_2Sr_2Ca_2Cu_3O_{10}$

$Tl_2Ba_2Ca_2Cu_3O_{10}$

$TlBa_2Ca_2Cu_3O_9$

$HgBa_2Ca_2Cu_3O_9$



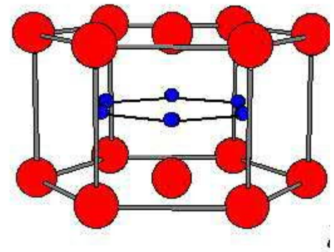
$$M_mA_2Q_{n-1}Cu_nO_{m+2+2n+\delta}$$

$$M\text{-}m2(n-1)n$$

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 Ti	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:
MgB_2



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