LECTURE SCHEDULE

Mon	(Ke3)	12.15 – 14.00
Wed	(Ke2)	10.15 – 12.00
Fri	(Ke5)	10.15 – 12.00

		Date	Topic
1.	Wed	06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri	08.09.	Short Survey of Main Group Elements
3.	Mon	11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed	13.09.	Transition Metals: General Aspects & Pigments
5.	Fri	15.09.	Redox Chemistry
6.	Mon	18.09.	Crystal Field Theory (Linda Sederholm)
7.	Wed	20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon	25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed	27.09.	Mn, Fe, Co, Ni, Cu & Magnetism
10.	Fri	29.09.	Cu & Superconductivity
11.	Mon	02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed	04.10.	Lanthanoids + Actinoids & Luminescence
13.	Fri	06.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri	13.10.	Inorganic Materials Chemistry Research

EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2

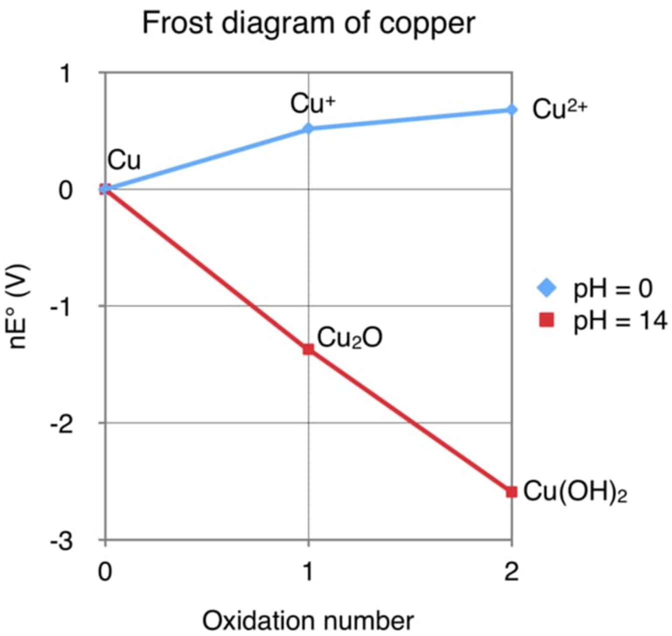
PRESENTATION TOPICS/SCHEDULE

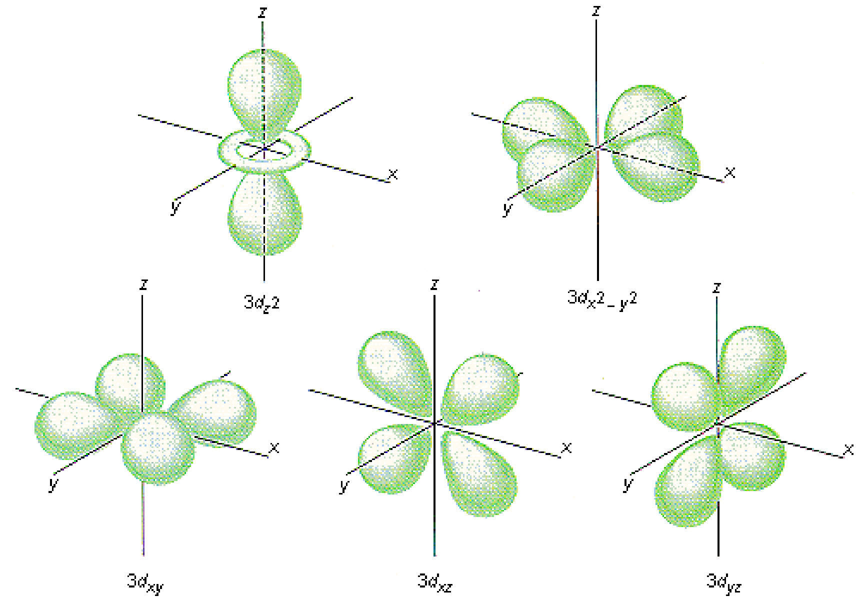
Mon	25.09.	Mo:	Maryam Jafarishiad & Saara Siekkinen
Wed	27.09.	Mn:	Naomi Lyle & Sanni Ilmaranta
		Ru:	Miklos Nemeszeghy & Timo de Jonge
Fri	29.09.	Cu:	Koshila Hiruni & Kaushalya Poonanoo
Wed	04.10.	Eu:	Binglu Wang & Mari
		Nd:	Patrich Wiesenfeldt & Tomoki Nakayama
		U:	Miikka Viirto & Ashish Singh
Fri	06.10.	Co:	Gabrielle Laurent & Yan Zheng
		In:	Sonja Alasaukko-oja & Katri Haapalinna
		Te:	Sofia Rantala & Roger Peltonen

QUESTIONS: Lecture 10

Which one(s) of the following materials are superconducting ?
Most importantly, explain/motivate each of your choices !

- Hg
- Cu
- CuO
- La_2CuO_4
- $La_2CuO_{4.1}$
- $(La_{0.9}Ba_{0.1})_2CuO_4$
- $HgBa_2Ca_2Cu_3O_{8.2}$



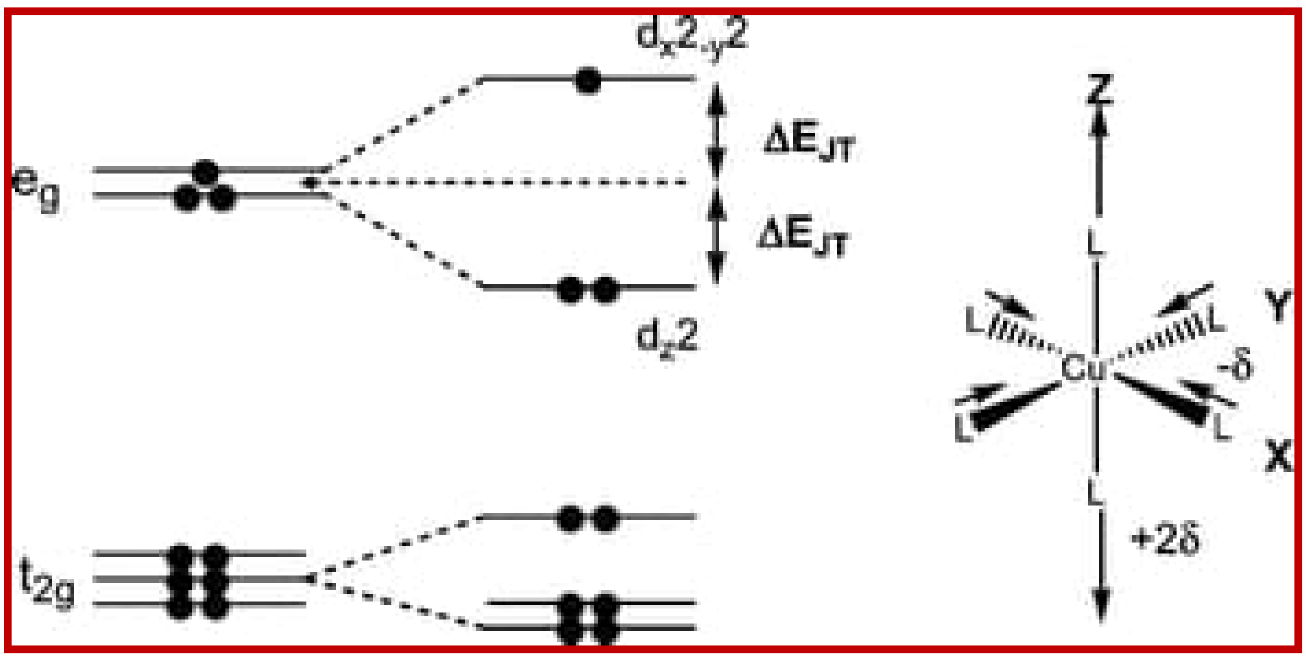


Cu: $4s^1\ 3d^{10}$

Cu⁺: $4s^0\ 3d^{10}$

Cu^{2+}: $4s^0\ 3d^9$

Cu^{3+}: $4s^0\ 3d^8$



COPPER

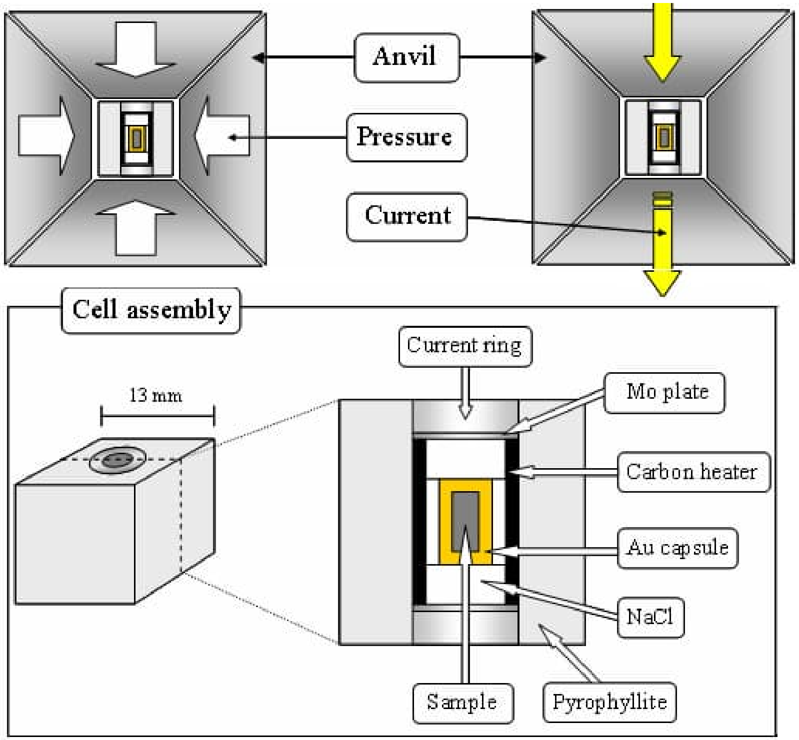
- **Known since 5000 BC:**

  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)**

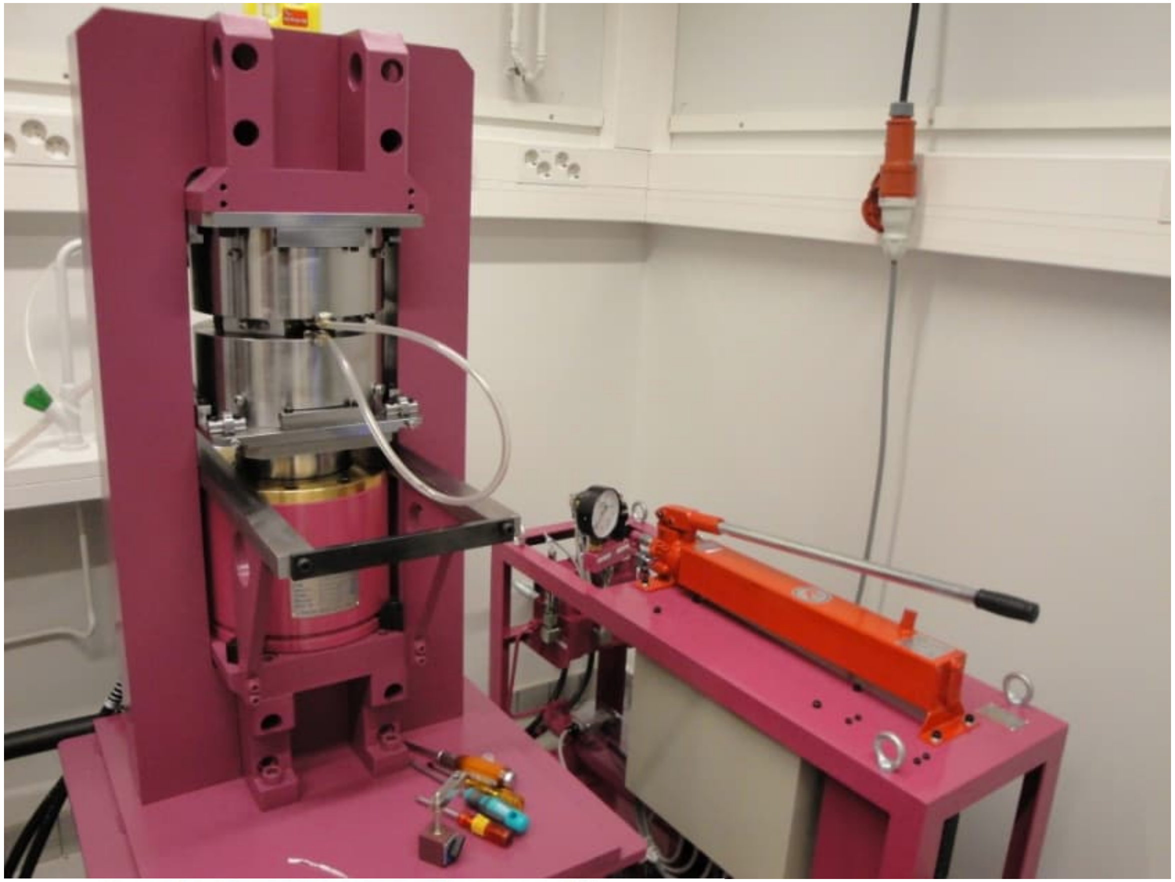


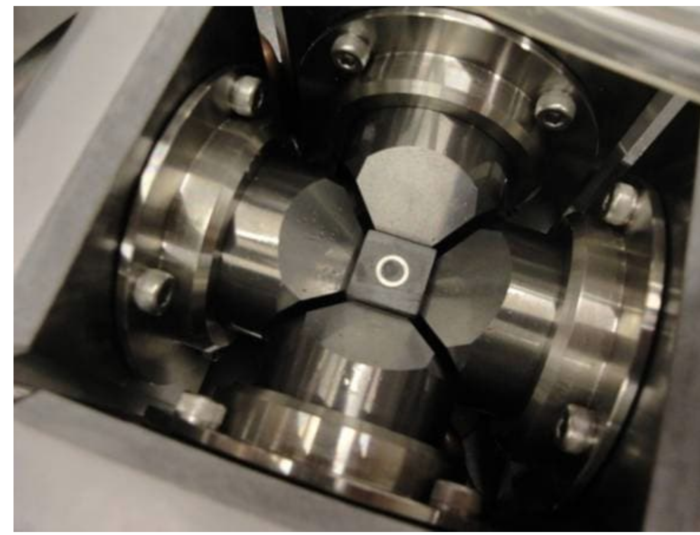
HIGH-PRESSURE SYNTHESIS

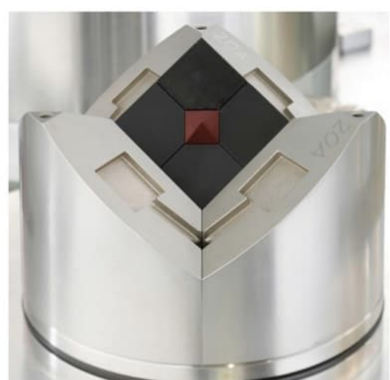
- 5 GPa = 50 000 atm
- 400 – 1200 ºC
- 10 – 120 min
- 50 – 100 mg

HP equipment
at Tokyo Tech

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





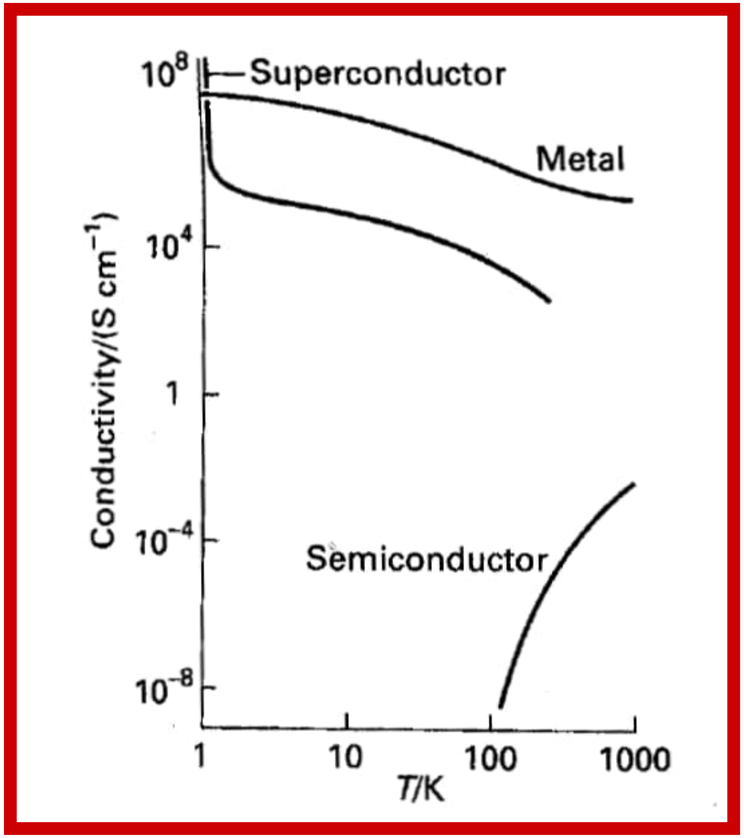



HP equipment at Aalto

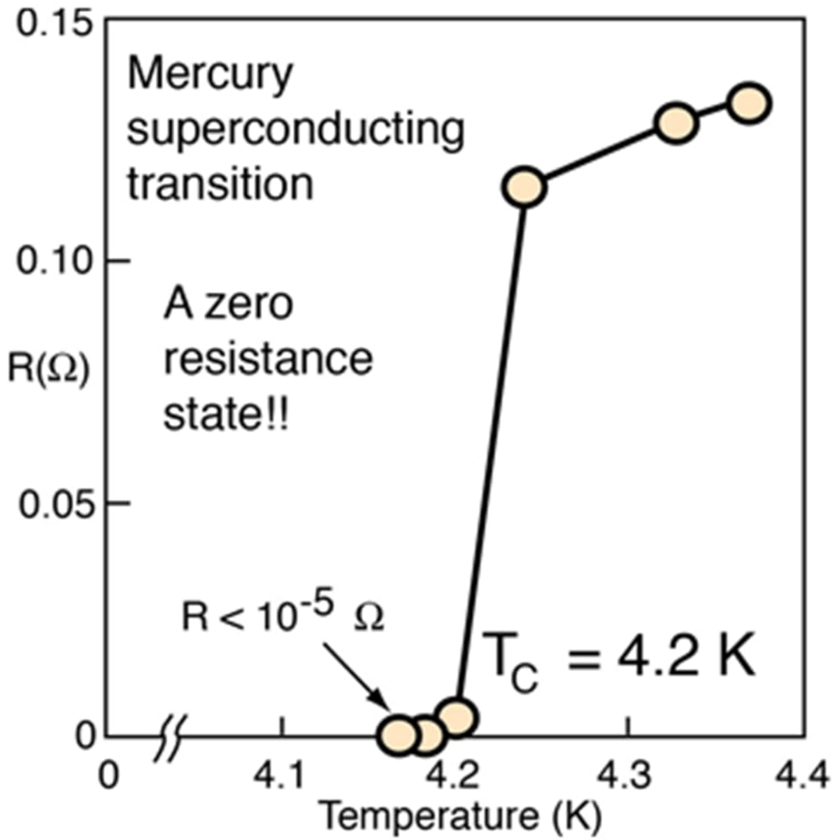
- 4 GPa & 25 GPa

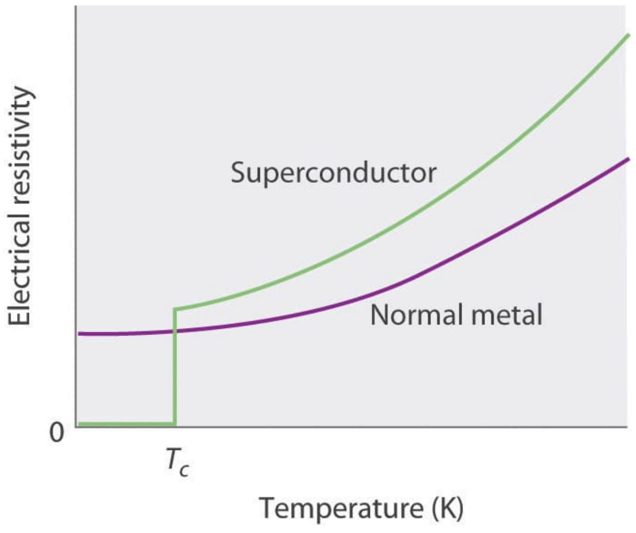
Superconductivity

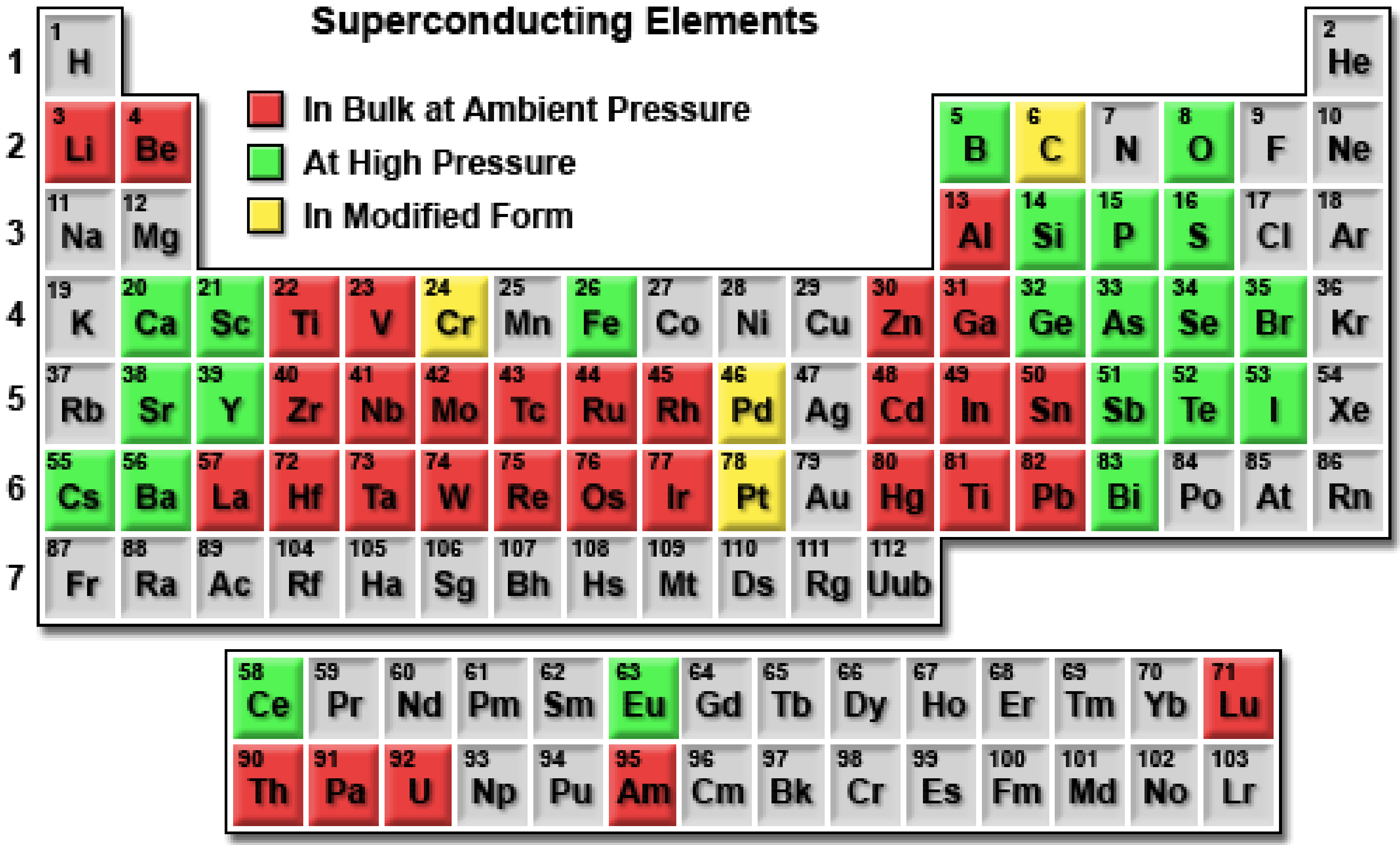
- 1911 Kamerlingh-Onnes
- $\rho = 0$



Nobel 1913

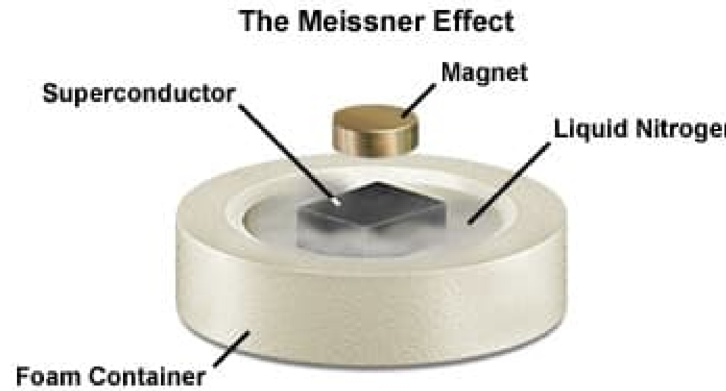





Superconducting Elements
In Bulk at Ambient Pressure
At High Pressure
In Modified Form
1 2 3 4 5 6 7
1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37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

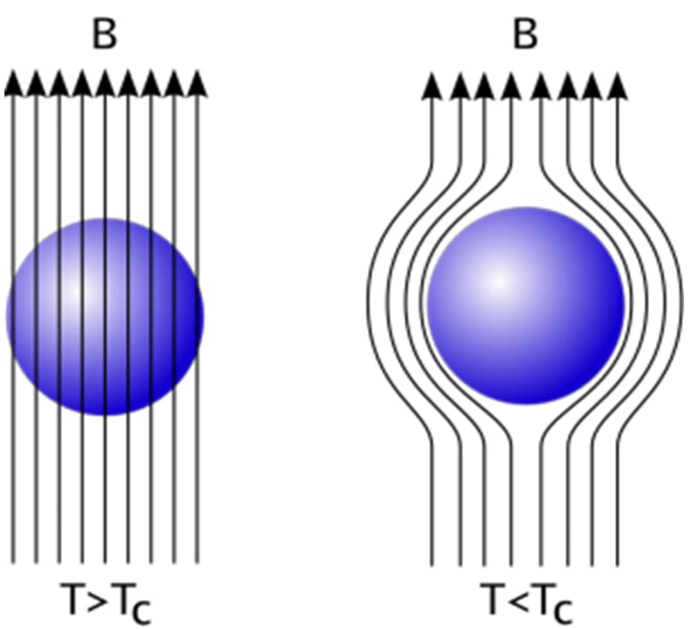
”Meissner effect”

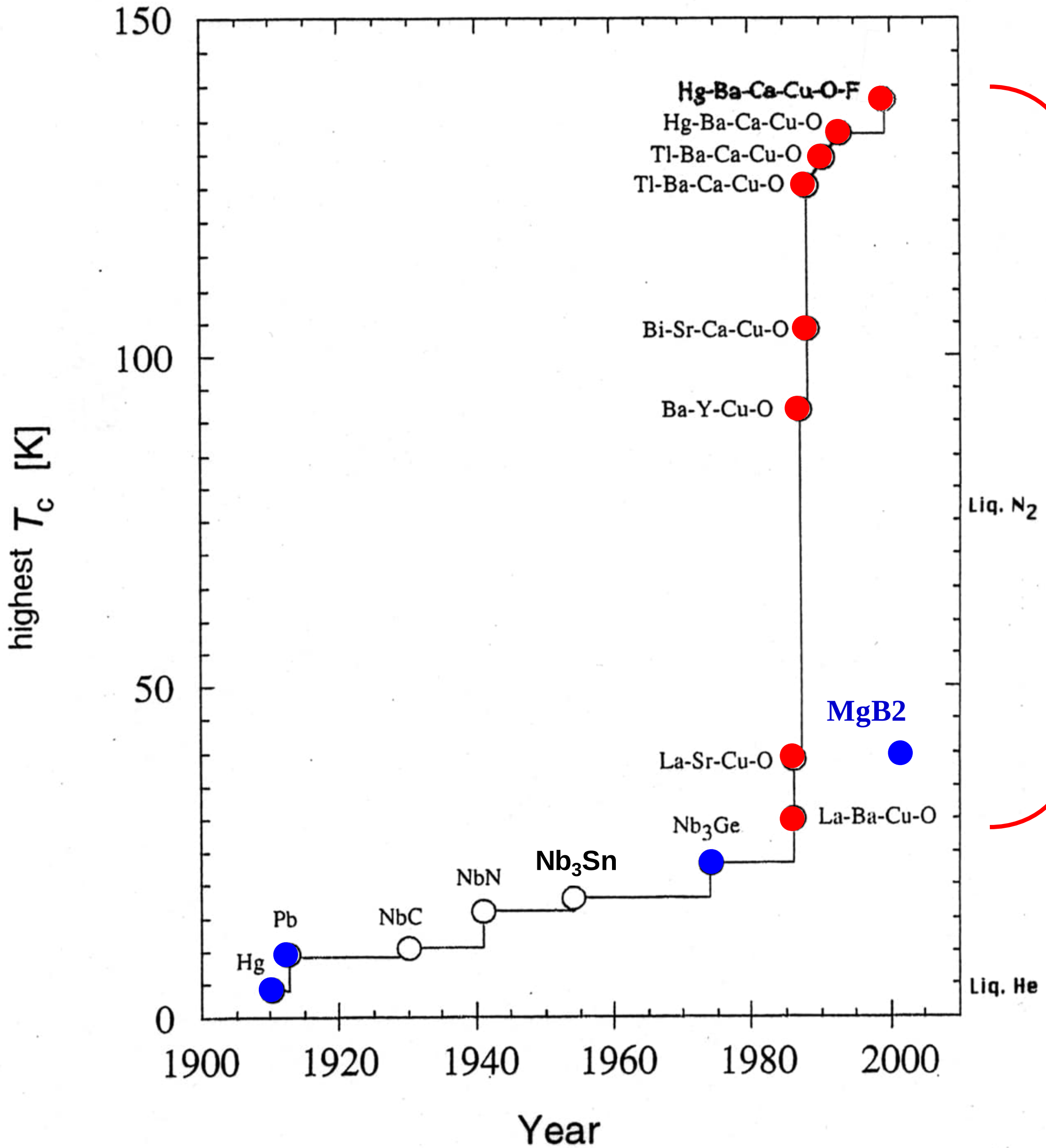
1933 Meissner and Ochenfeld:
$\chi = B/H < 0 \rightarrow$ levitation



Super-Maglev Train

- 603 km / hour
- Test line 42.8 km

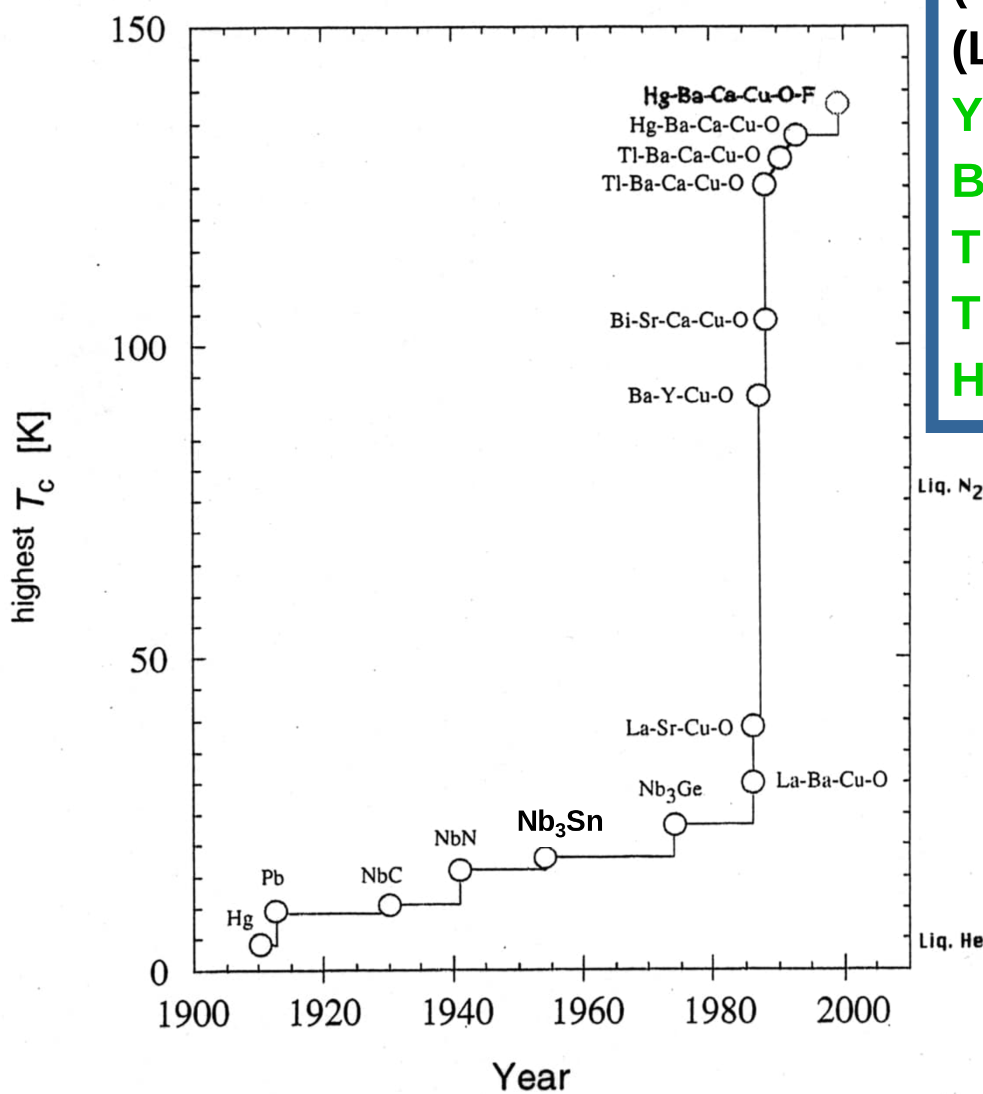




High-*Tc* superconductivity

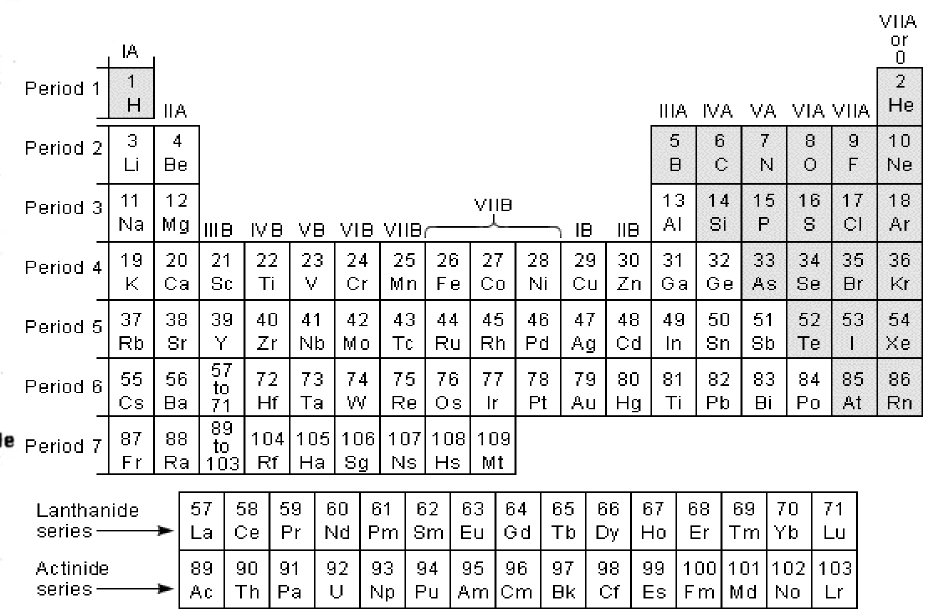
- 1986: Bednorz and Müller
- $(La,Ba)_2CuO_4$ T_c = ~30 K
- Nobel 1987

Search for new high-T_c superconductors

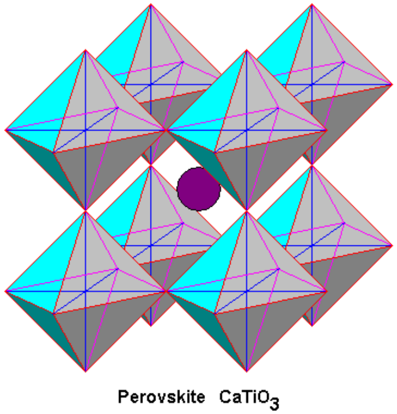


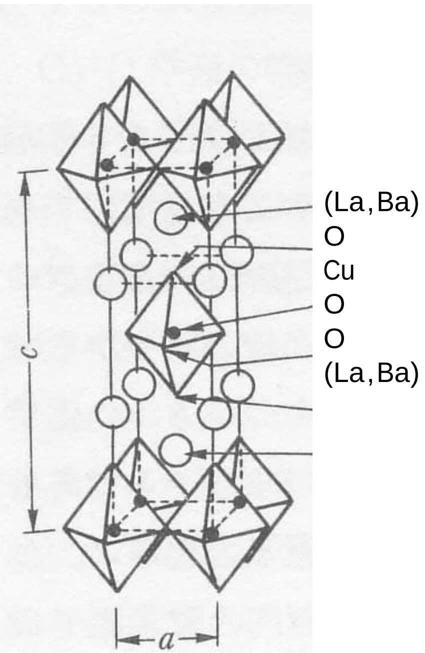
$(La_{0.92}Ba_{0.08})CuO_4$
$(La_{0.92}Sr_{0.08})_2CuO_4$
$YBa_2Cu_3O_7$
$Bi_2Sr_2Ca_2Cu_3O_{10}$
$Tl_2Ba_2Ca_2Cu_3O_{10}$
$TlBa_2Ca_2Cu_3O_9$
$HgBa_2Ca_2Cu_3O_9$

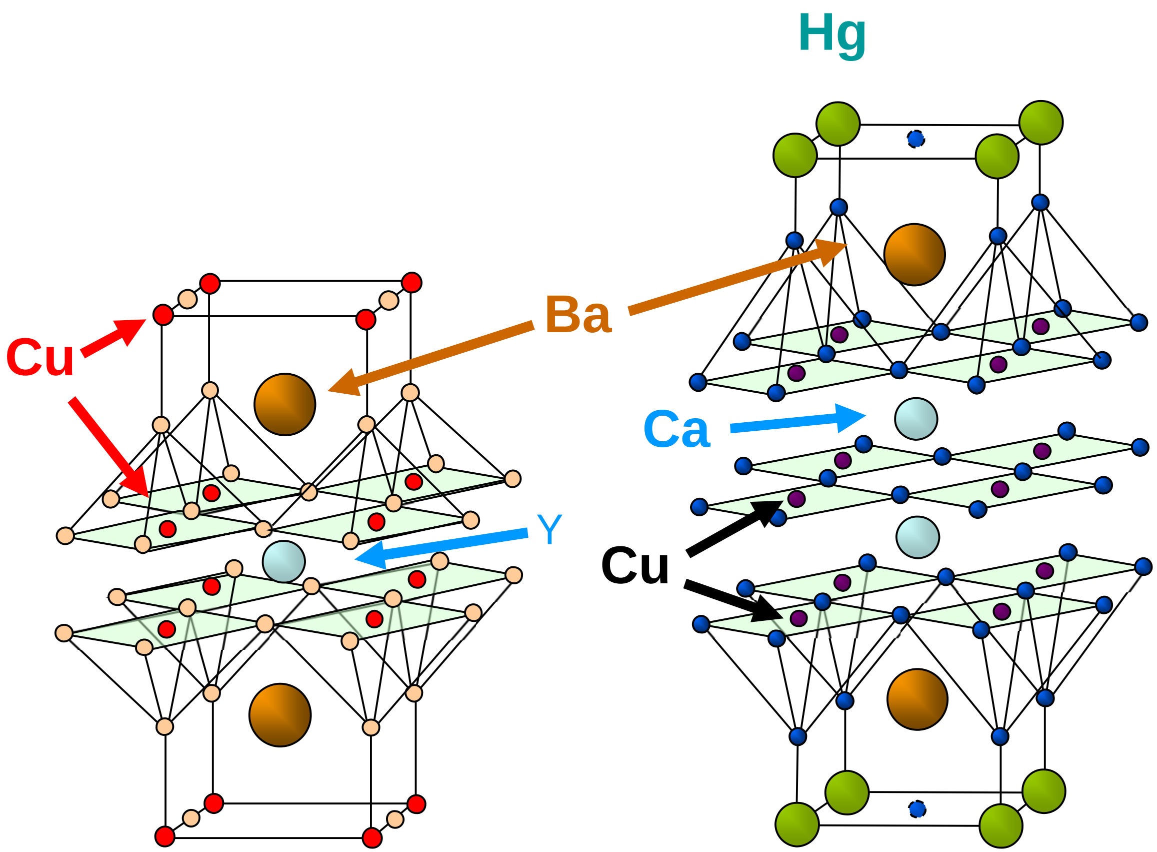
- **Chemical pressure**
- **Inert-pair effect**



Crystal Structures of High-T_c Superconductive Copper Oxides - Jahn-Teller distorted Cu(II/III) -







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

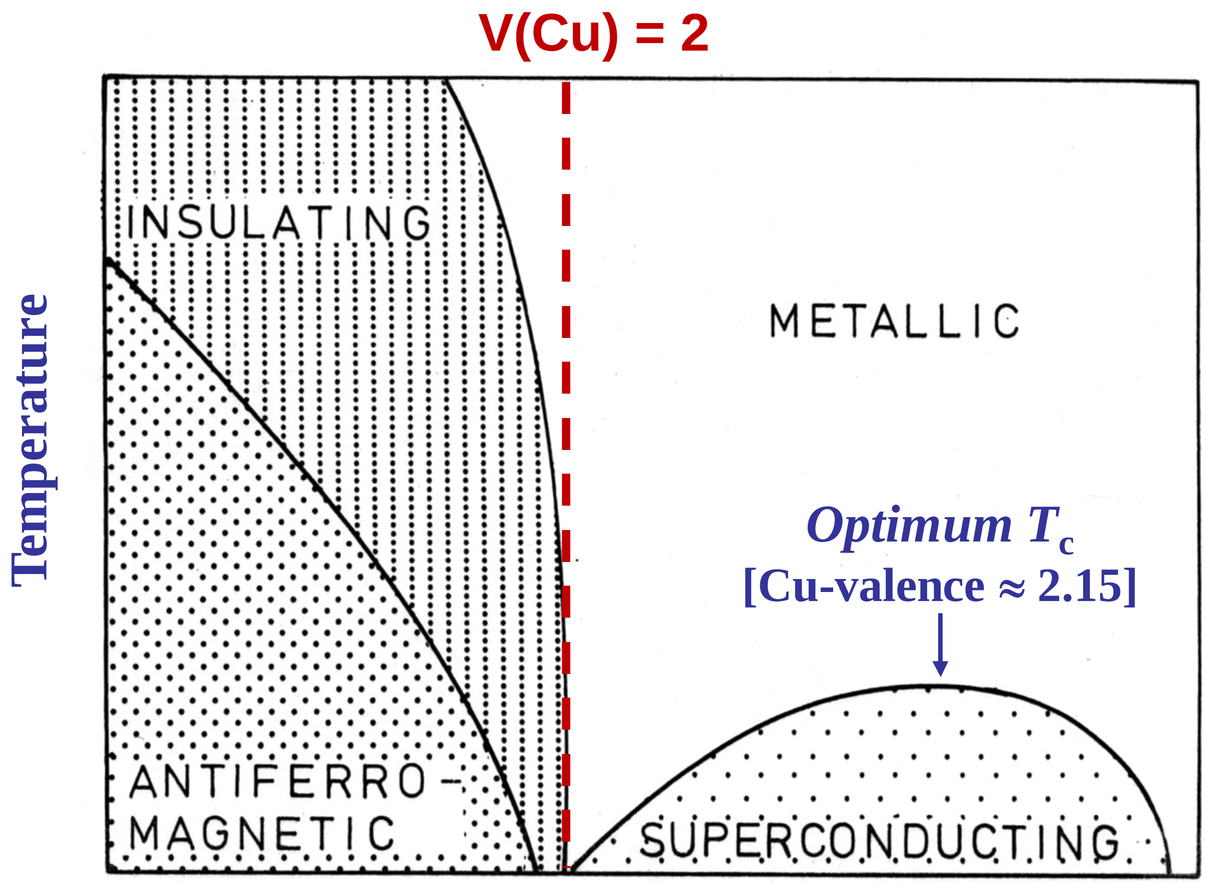
$T_c \approx 35$ K

$YBa_2Cu_3O_{7-\delta}$

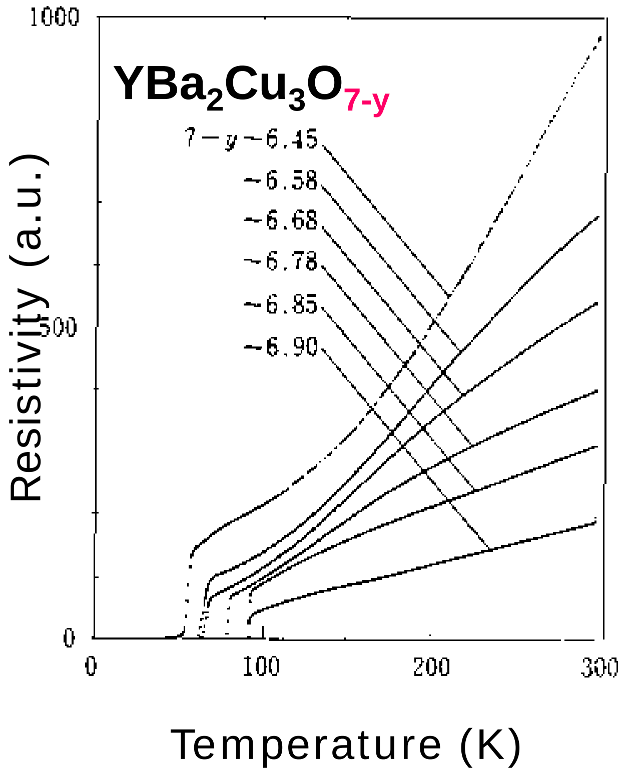
$T_c \approx 92$ K

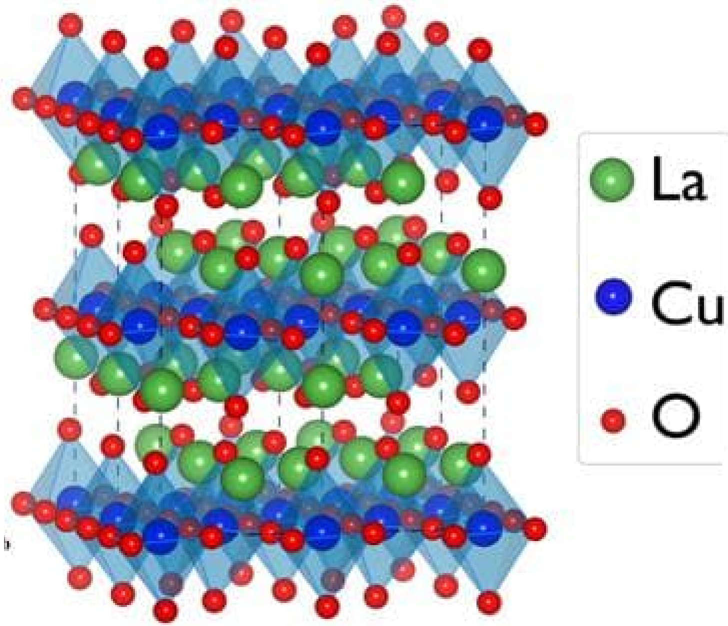
$HgBa_2Ca_2Cu_3O_{9-\delta}$

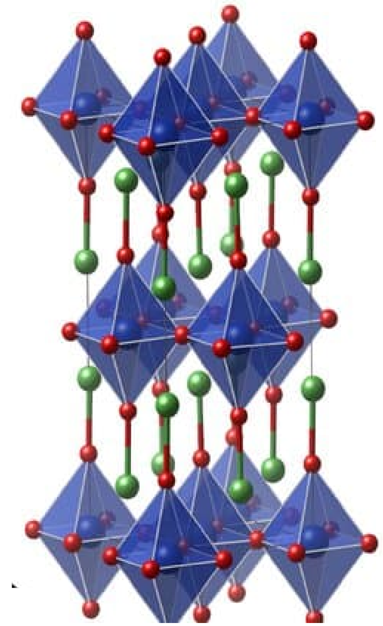
$T_c \approx 135$ K

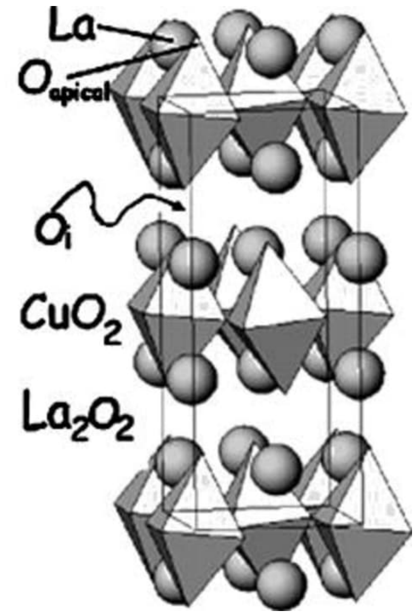


Valence of copper in CuO_2 planes
(p-type conductors: hole carrier concentration)







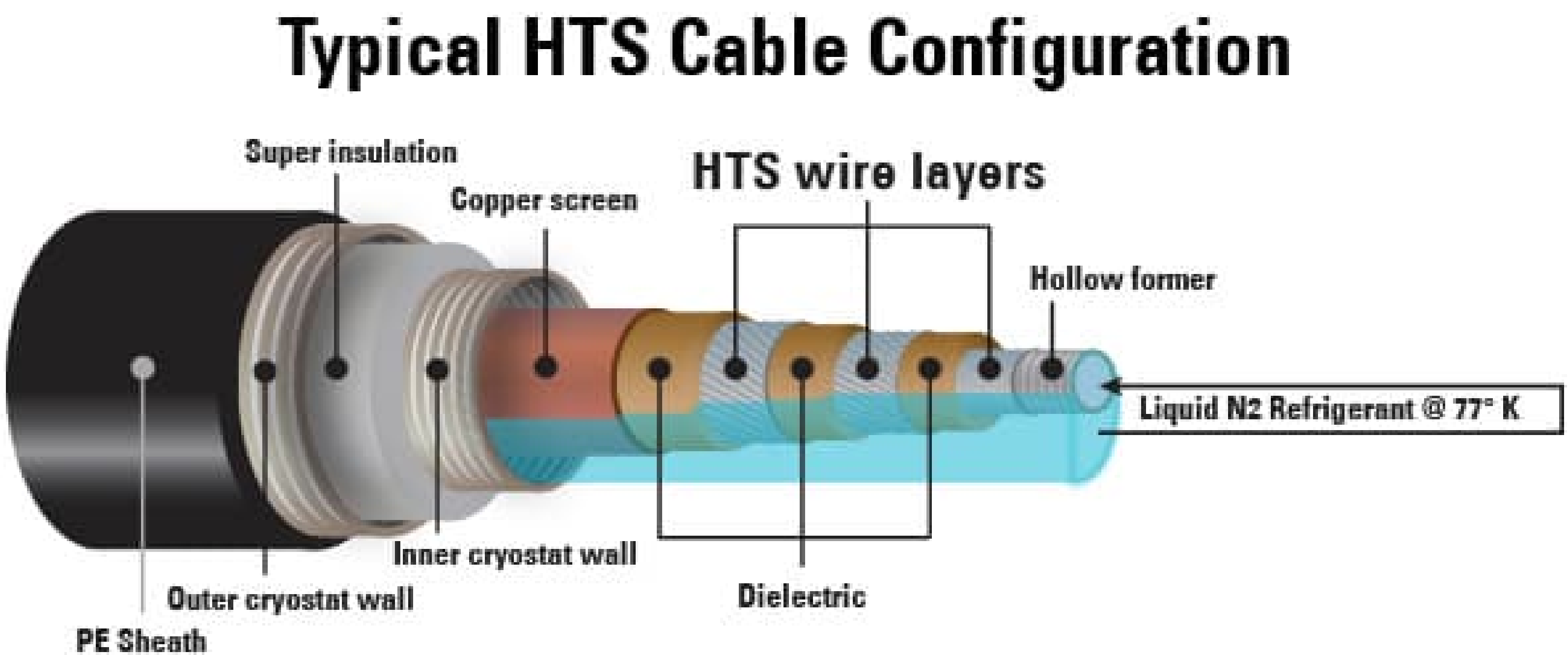


La_2CuO_4

- **What is the copper valence in this compound ?**
- **Is this compound superconducting ?**
- **How to increase hole concentration (= increase Cu valence) ?**

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)



APPLICATIONS of ELECTROMAGNETS

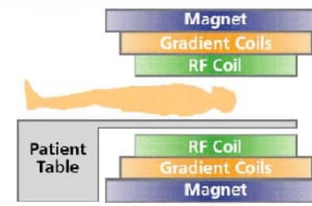
Superconducting Magnets

- 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.



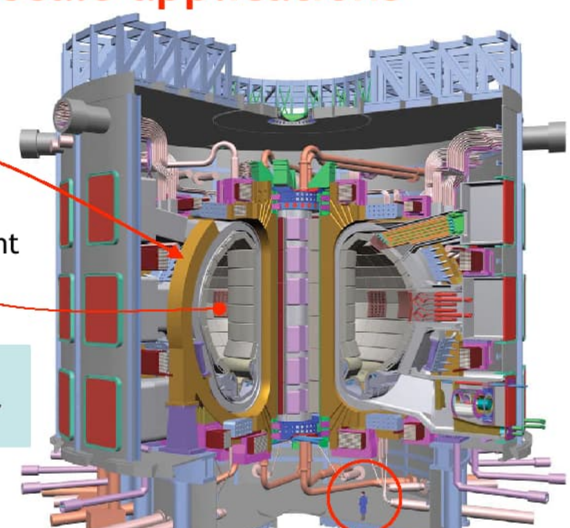
900 MHz NMR (UW Chemistry)

21.7 T field

Large scale applications

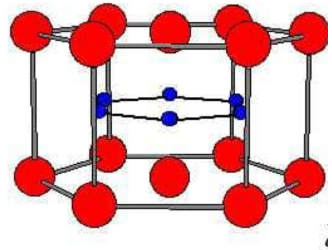
Superconducting magnet

Plasma confinement torus



Proposed ITER fusion test reactor

Akimitsu 2001: MgB_2



Hosono 2006 → [La(O,F)][FeAs]