Functional Inorganic Materials
Fall 2021

Tuesdays: 14.15 - 16.00
Thursdays: 12.15 - 14.00
Remote Zoom lectures

#	Date	Who	Topic
1	Tue 02.11.	Maarit	Introduction + Materials design
2	Thu 04.11.	Antti	Computational materials design
3	**Tue 09.11.**	**Maarit**	**Superconductivity: High-T_c superconducting Cu oxides**
4	Thu 11.11.	Maarit	Ionic conductivity (Oxygen): Oxygen storage and SOFC
5	Tue 16.11.	Maarit	Ionic conductivity (Lithium): Li-ion battery
6	Thu 18.11.	Antti	Thermal conductivity
7	Tue 23.11.	Antti	Thermoelectricity
8	Thu 25.11.	Maarit	Hybrid materials
9	Tue 30.11.	Maarit	Luminescence and optically active materials
10	Thu 02.12.	Antti	Piezoelectricity
11	Tue 07.12.	Antti	Pyroelectricity and ferroelectricity
12	Thu 09.12.	Antti	Magnetic and multiferroic oxides

LECTURE 3: (High-T_c) Superconductivity

- Zero resistance, Meissner effect, Cooper pair, Josephson junction
- History & Impact
- Physics – Materials/Chemistry – Technology
- New-material discoveries: Design principles & Good luck
- Perovskite & Ruddlesden-Popper
- Multi-layered crystal structure & Homologous series
- Aliovalent substitution / Isovalent substitution (= Chemical pressure)
- Mixed-valency & Oxygen nonstoichiometry
- p-type & n-type: Importance of Cu coordination number/sphere

LECTURE EXERCISE 3

1. **The following copper oxide compounds are high-T_c superconductors: $YBa_2Cu_3O_{7\pm\delta}$, $Bi_2Sr_2CuO_{6\pm\delta}$, $Bi_2Sr_2CaCu_2O_{8\pm\delta}$ and $Bi_2Sr_2Ca_2Cu_3O_{10\pm\delta}$**

   a) Give the systematic name (= chemical formula abbreviation) for each compound.

   b) Which of the compounds should have the highest T_c (when optimized); give the reason for your choice!

   c) Explain the importance of oxygen nonstoichiometry parameter δ for these compounds.

   d) Explain why a multilayered crystal structure is useful for the high-T_c copper-oxide superconductors.

2. **Nb_3Sn and Sn_3Ge are important ”low-temperature” superconductors and members of the so-called ”A15 family” of intermetallic compounds. Please make a quick/small literature search (3-7 references) to discuss few aspects (history, different characteristics, etc.) which you find most interesting related to these materials.**

PHYSICAL REVIEW VOLUME 95, NUMBER 6 SEPTEMBER 15, 1954

Superconductivity of Nb_3Sn

B. T. Matthias, T. H. Geballe, S. Geller, and E. Corenzwit
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received June 10, 1954)

Intermetallic compounds of niobium and tantalum with tin have been found. The superconducting transition temperature of Nb_3Sn at 18°K is the highest one known.

Ted Geballe 100 years
Jan. 2020

SOME intermetallic compounds crystallizing with the β-wolfram structure become superconducting, as was first pointed out by Hardy and Hulm.[1] In particular one of these, V_3Si, showed a remarkably high transition temperature between 16.9°K and 17.1°K. These authors made various attempts to raise this temperature by introducing a third component but were not successful.

The β-wolfram structure is a very peculiar structure with rather varying interatomic distances,[2] a fact which may render the addition of a third component rather difficult. It seemed therefore more favorable to look for another β-W compound with a large volume and a favorable electron/atom ratio[3] in order to raise the superconducting transition temperature. There is very little known about the systematic occurrence of intermetallic compounds in this β-W structure. The fact that thus far no niobium compounds have been reported seemed therefore not significant.

It was expected that in the Nb-Sn and Ta-Sn this crystal form would be found, an assumption which was verified. We have determined that Nb_3Sn and Ta_3Sn both crystallize in a β-W structure with a lattice constant of about 5.3A. The Ta_3Sn was measured in the apparatus previously described,[4] and became superconducting near 6°K. The transition temperature of the Nb_3Sn was determined by immersing the sample surrounded by a copper coil in liquid hydrogen. The self-inductance of the coil was measured on a General Radio Model 650A Bridge at 1 kc/sec as the sample was slowly cooled. Figure 1 shows the results for two different samples made under somewhat different conditions which were cooled from 18.5°K to 17.5°K during a period of about 30 minutes. The sharpness of the transition together with the reproducibility between samples indicates that these samples are indeed well-defined compounds. The onset of superconductivity at 18.05°K±0.1° is determined by extrapolating the line of steepest slope to the high temperature line. Temperatures were measured by a copper constantan thermocouple secured to the measuring coil and independently checked with the vapor pressure of hydrogen.

APPENDIX

While the synthesis of an intermetallic compound is generally a rather straightforward process, it may be necessary to describe briefly the formation of these compounds. No reference to Nb-Sn or Ta-Sn was found in the literature. The melting point of niobium is nearly 400° above the boiling point of tin, and an arc furnace is therefore out of place. A complete reaction can, however, easily be obtained by having molten tin run over Nb or Ta powder in a closed-off quartz tube at 1200°C. Nb_3Sn and Ta_3Sn seem to be formed by a peritectic reaction between 1200°C and 1550°C.

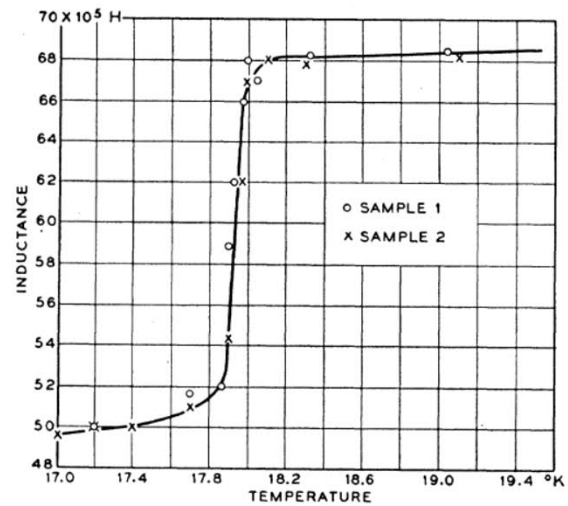
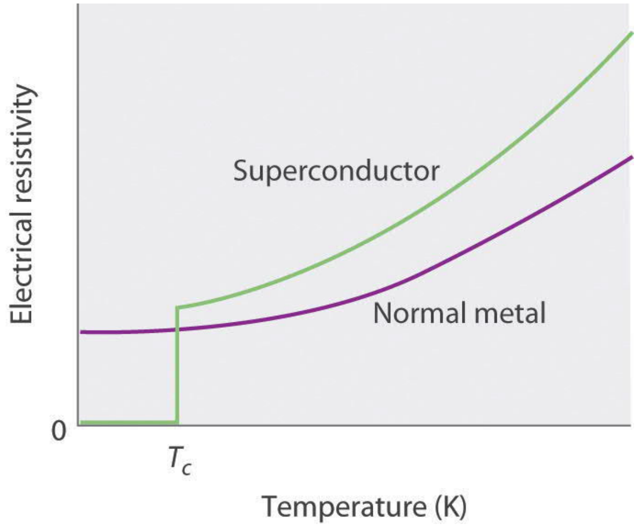
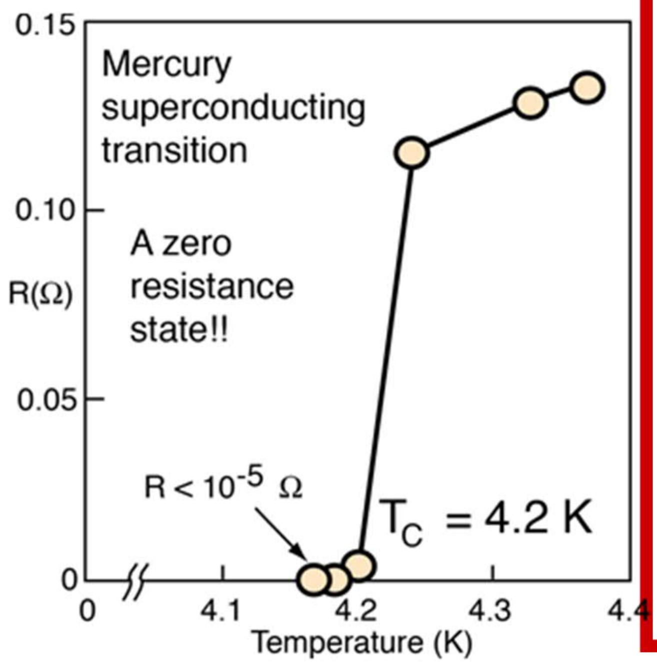
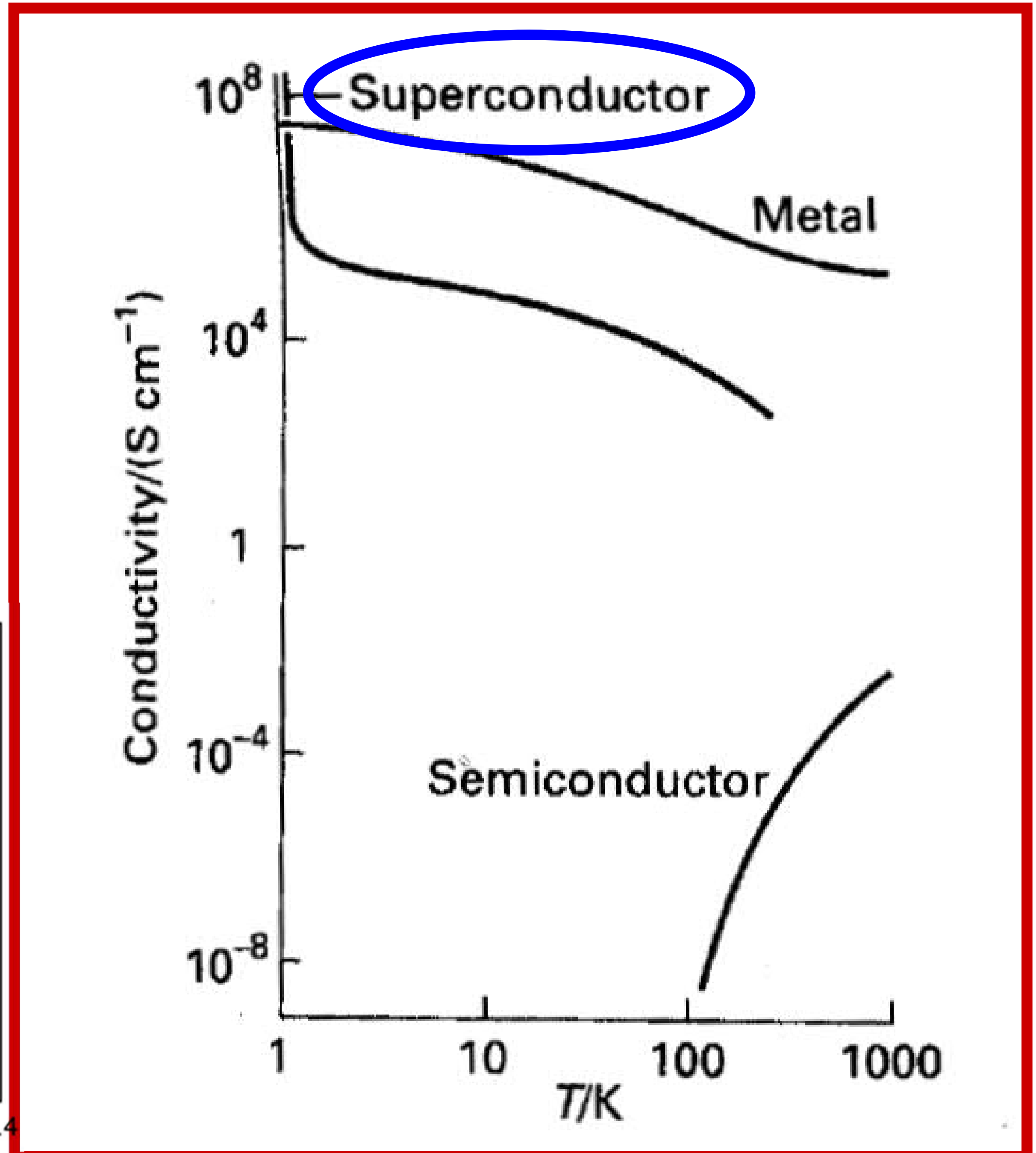


Fig. 1. Variation of susceptibility with temperature of Nb_3Sn.

[1] G. Hardy and J. K. Hulm, Phys. Rev. **89**, 884 (1953).
[2] H. I. Wallbaum, Z. Metallkunde **31**, 362 (1939).
[3] B. T. Matthias, Phys. Rev. **92**, 874 (1953).
[4] B. T. Matthias and J. K. Hulm, Phys. Rev. **87**, 799 (1952).


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
Conductivity/(S cm^-1)
10^8
10^4
1
10^-4
10^-8
1
10
100
1000
T/K

SUPERCONDUCTIVITY

Superconductivity

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

Nobel 1913

Meissner effect

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

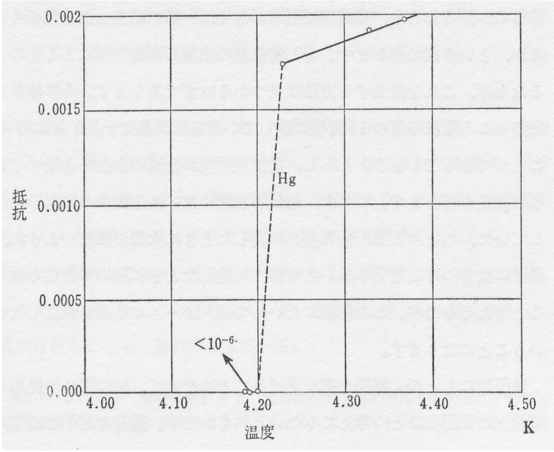
High-T_c superconductivity

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

Present record in T_c:

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

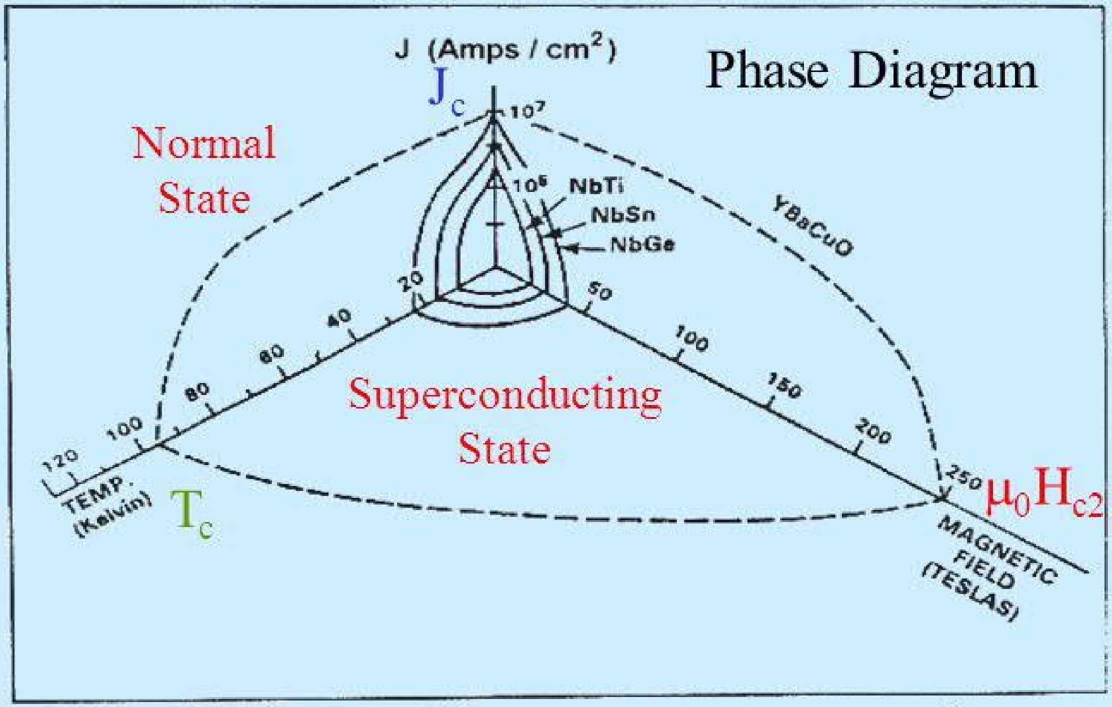
Nobel 1987



Kamerlingh-Onnes Institute,
@University of Leiden, the Netherlands

Heike Kamerlingh-Onnes and J.D. van der Waals

What are the Limits of Superconductivity?



$$f_{\text{super}} = f_{\text{normal}} + \alpha(T)|\psi|^2 + \frac{\beta(T)}{2}|\psi|^4 + \frac{1}{2m^*}\left|\left(\frac{\hbar}{i}\vec{\nabla} - e^*\vec{A}\right)\psi\right|^2 + \frac{\mu_0 h^2}{2}$$

Ginzburg-Landau free energy density

Temperature dependence

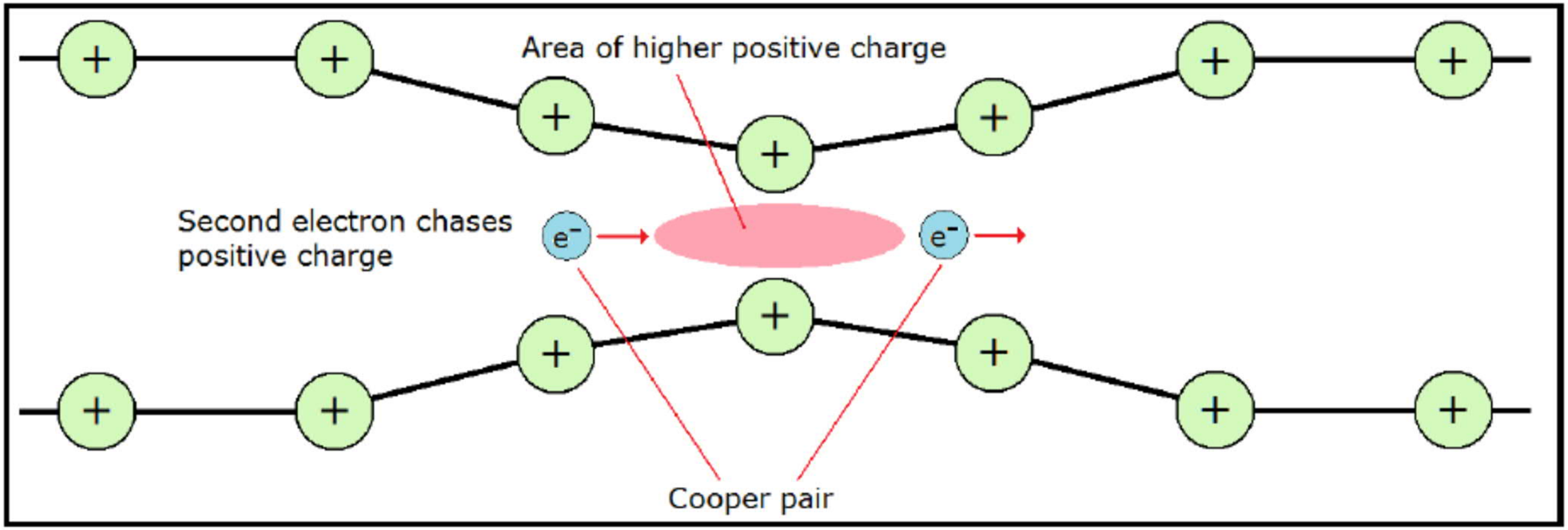
Currents

Applied magnetic field

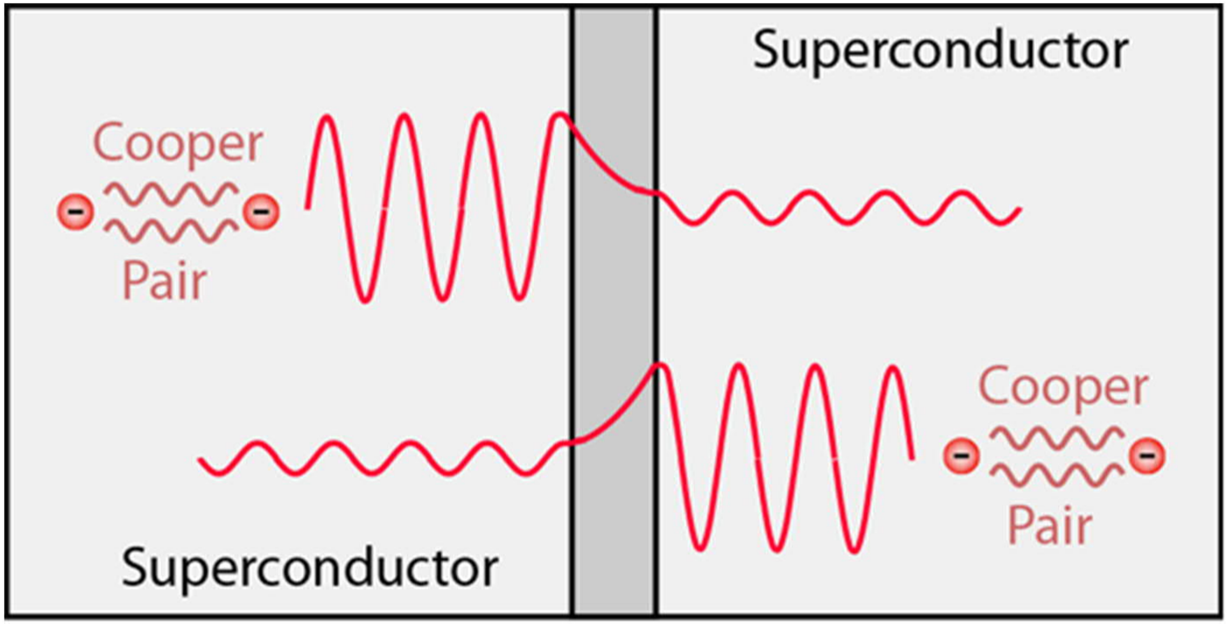
UNIVERSITY OF MARYLAND

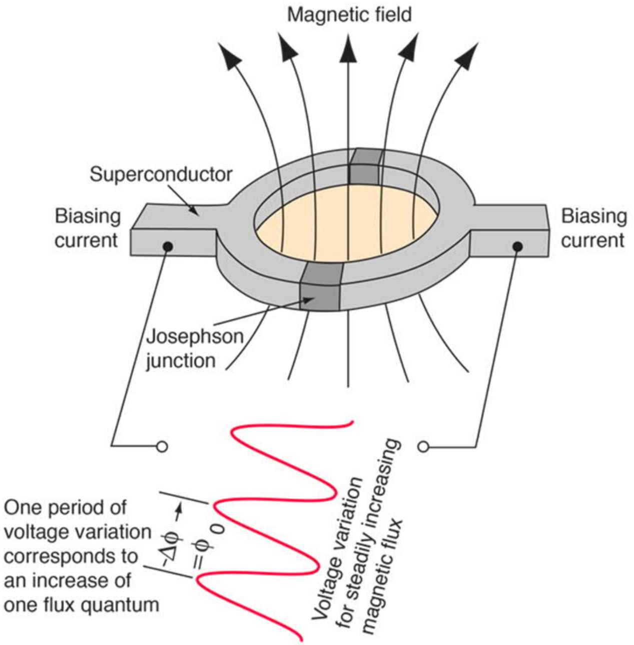
Bardeen, Cooper & Schrieffer

- BCS theory 1957
- Nobel 1972
- Cooper pairs
- Coupled through Phonons in convential superconductors



https://dc.edu.au/wp-content/uploads/cooper-pair-phonon.png



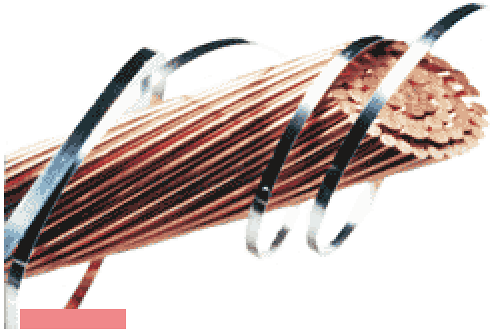


Josephson Junction & SQUID

- 1962 Brian David Josephson (Nobel 1973)
- Two superconductors separated by a thin insulating layer
- Tunneling of Cooper pairs through the junction
- Macroscopic quantum effect
- Josephson junction device has become the standard measure of voltage
- Superconducting quantum interference device (SQUID) based on Josephson junctions: measurement of extremely weak signals (e.g. subtle changes in the human body's electromagnetic energy field)

Application Examples of (high-T_c) Superconductors

- Cables and wires ($\rho = 0$)
  → public power supply (Copenhagen 2001)



- Strong magnets ($\rho = 0$)

- Microwave filters ($\rho = 0$)
  → to improve signal reception
  in wireless phone towers

- Levitation (Meissner)
  → "True" MAGLEV trains

- Sensitive magnetic probes (Josephson)

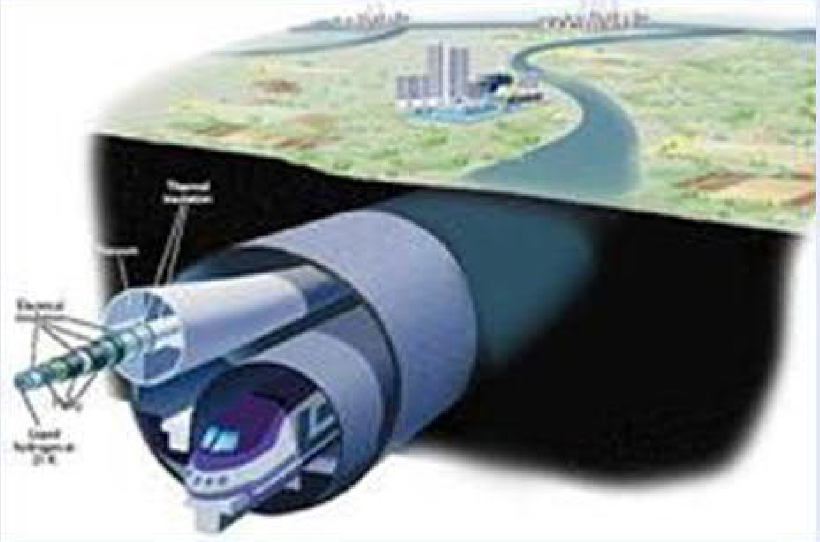
→ SQUID, NMR, MRI

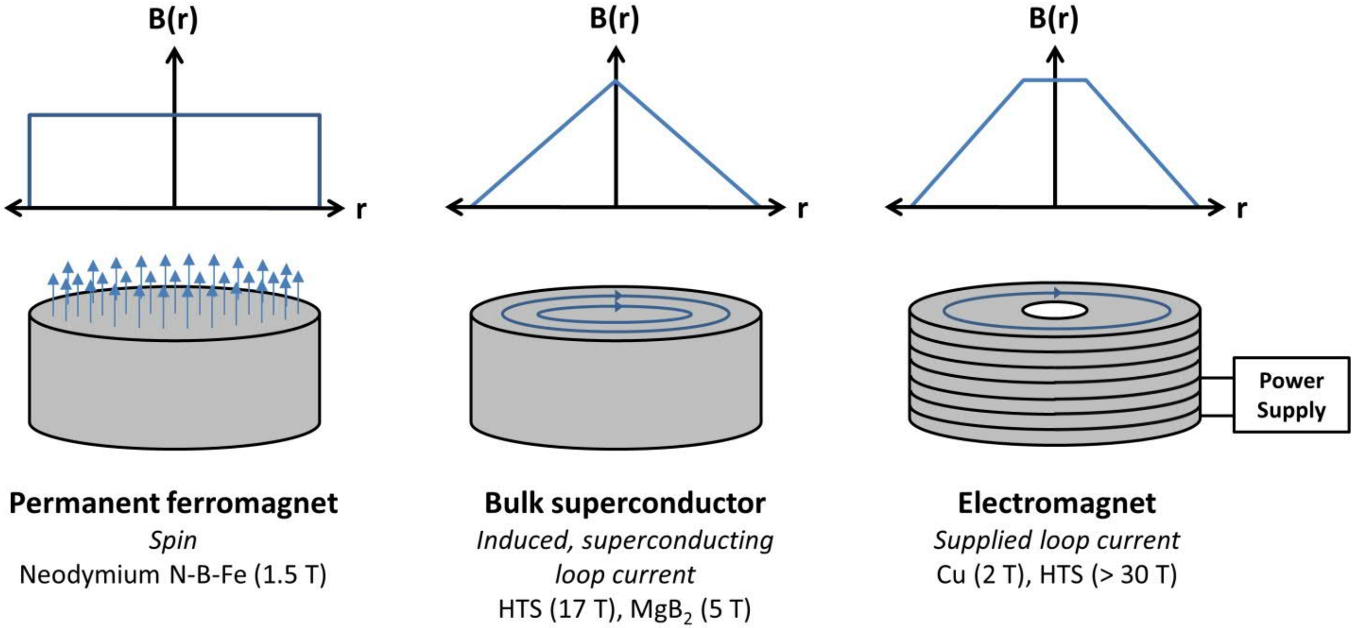
- Supercomputers (Josephson)

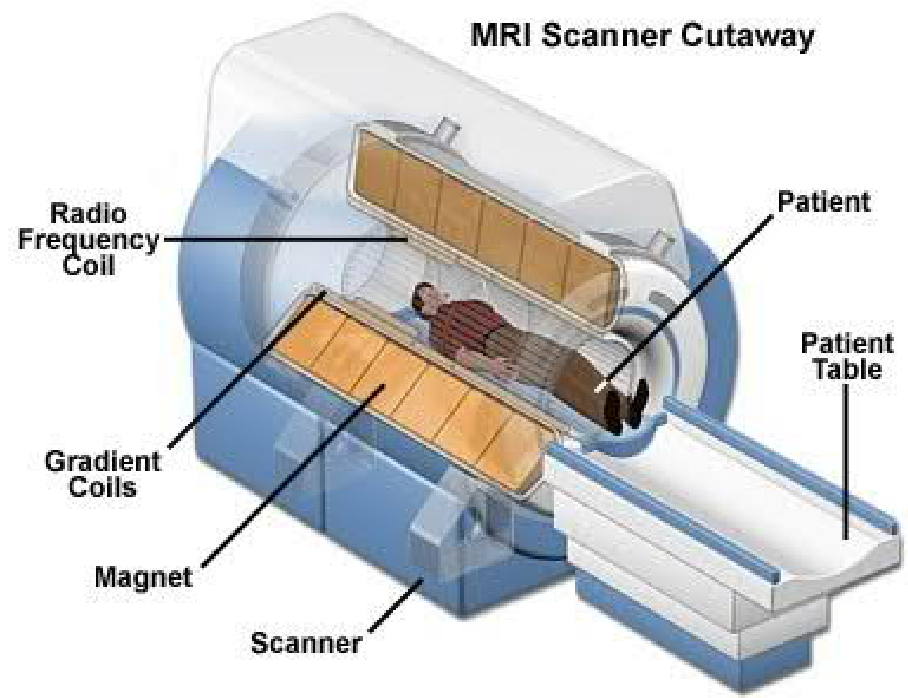
Applications using Superconductors

Superconducting power transmission

- currently we waste ~ 20 % of our energy just transporting it around
- potentially the next industrial revolution

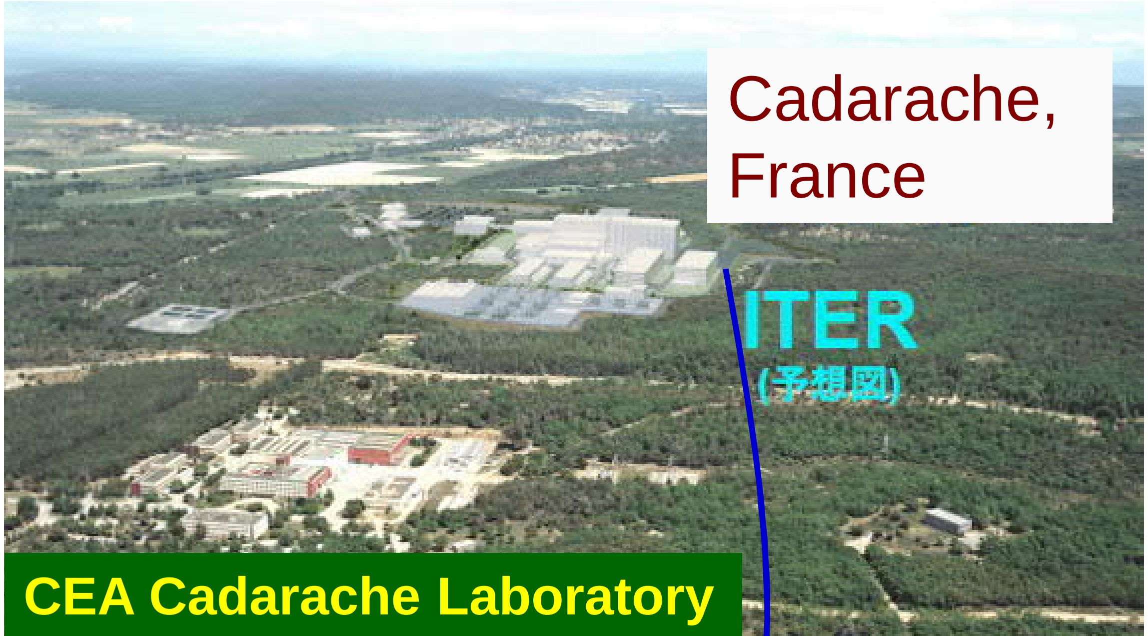



B(r)
r
B(r)
r
B(r)
r
Power Supply
Permanent ferromagnet
Spin
Neodymium N-B-Fe (1.5 T)
Bulk superconductor
Induced, superconducting loop current
HTS (17 T), MgB_2 (5 T)
Electromagnet
Supplied loop current
Cu (2 T), HTS (> 30 T)


MRI Scanner Cutaway
Radio Frequency Coil
Patient
Patient Table
Gradient Coils
Magnet
Scanner

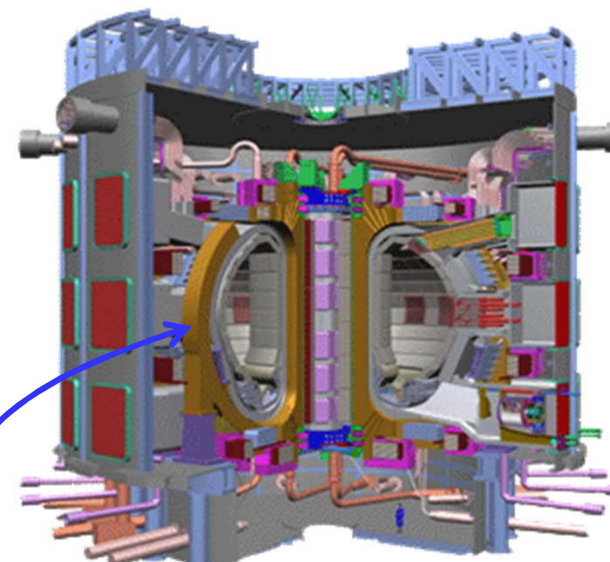
ITER: International Thermonuclear Experimental Reactor

since October, 2007

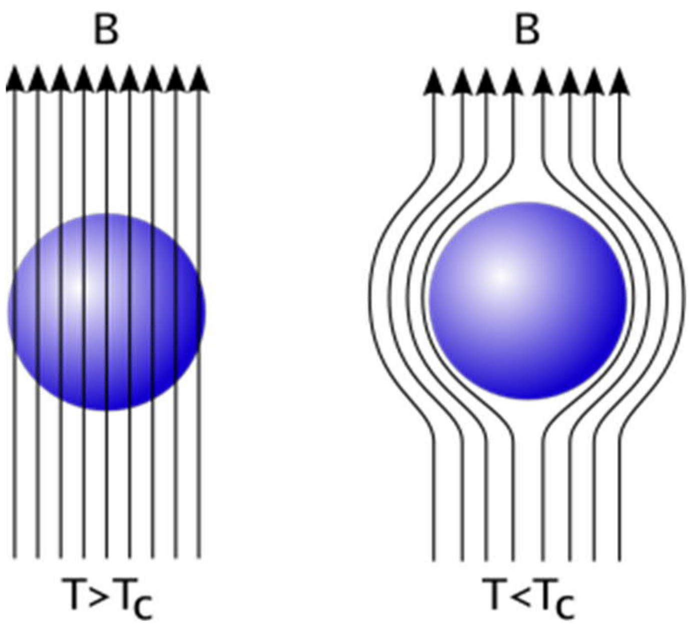


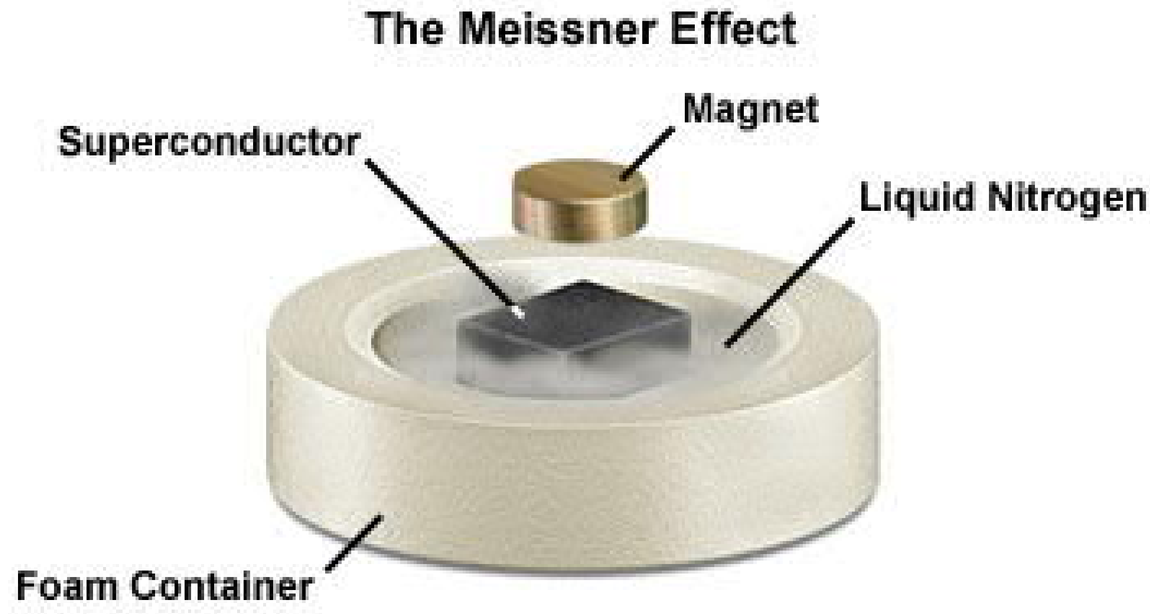
NbTi or Nb_3Sn

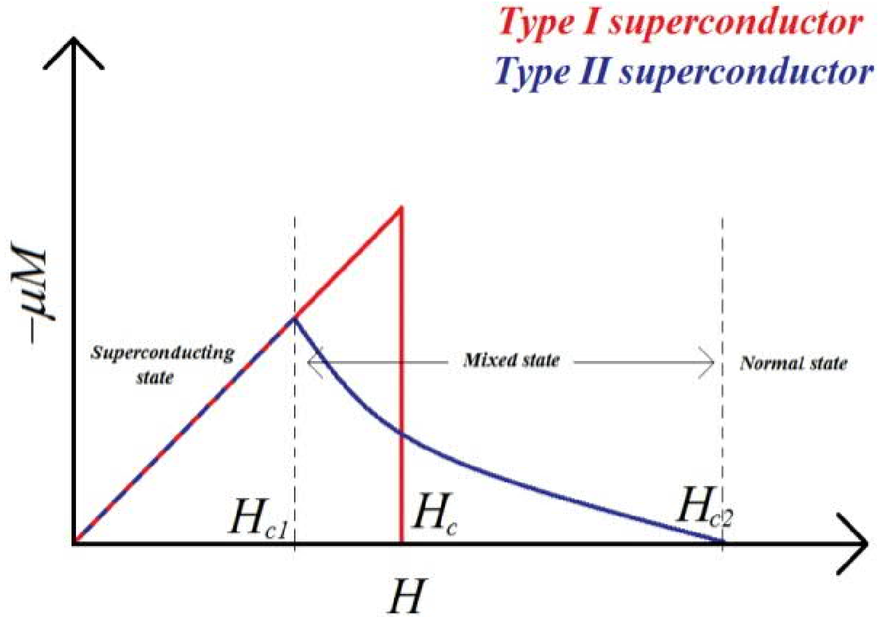
Nuclear Fusion Reactor



Superconducting Magnets

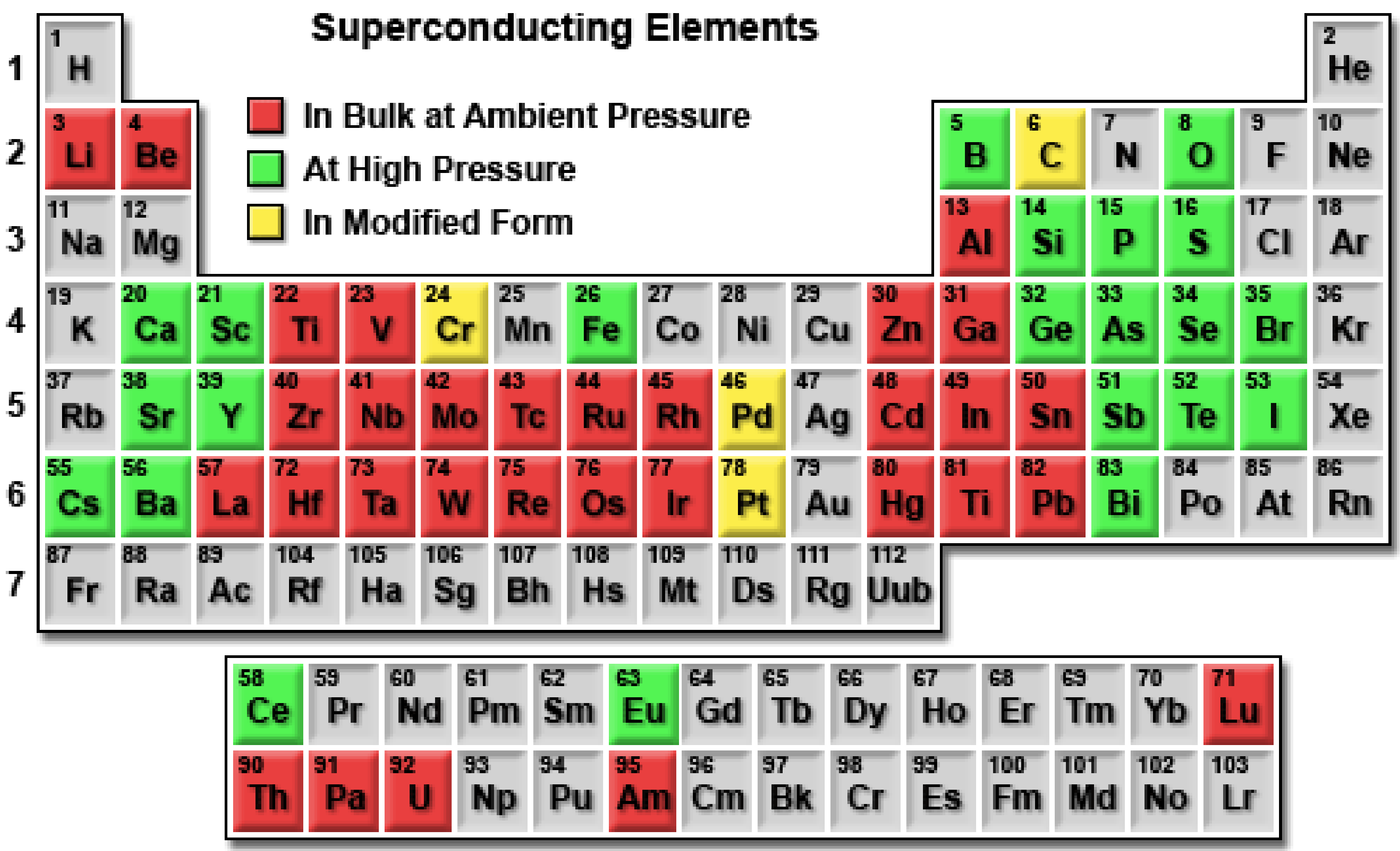

B
B
T>T$_C$
T<T$_C$

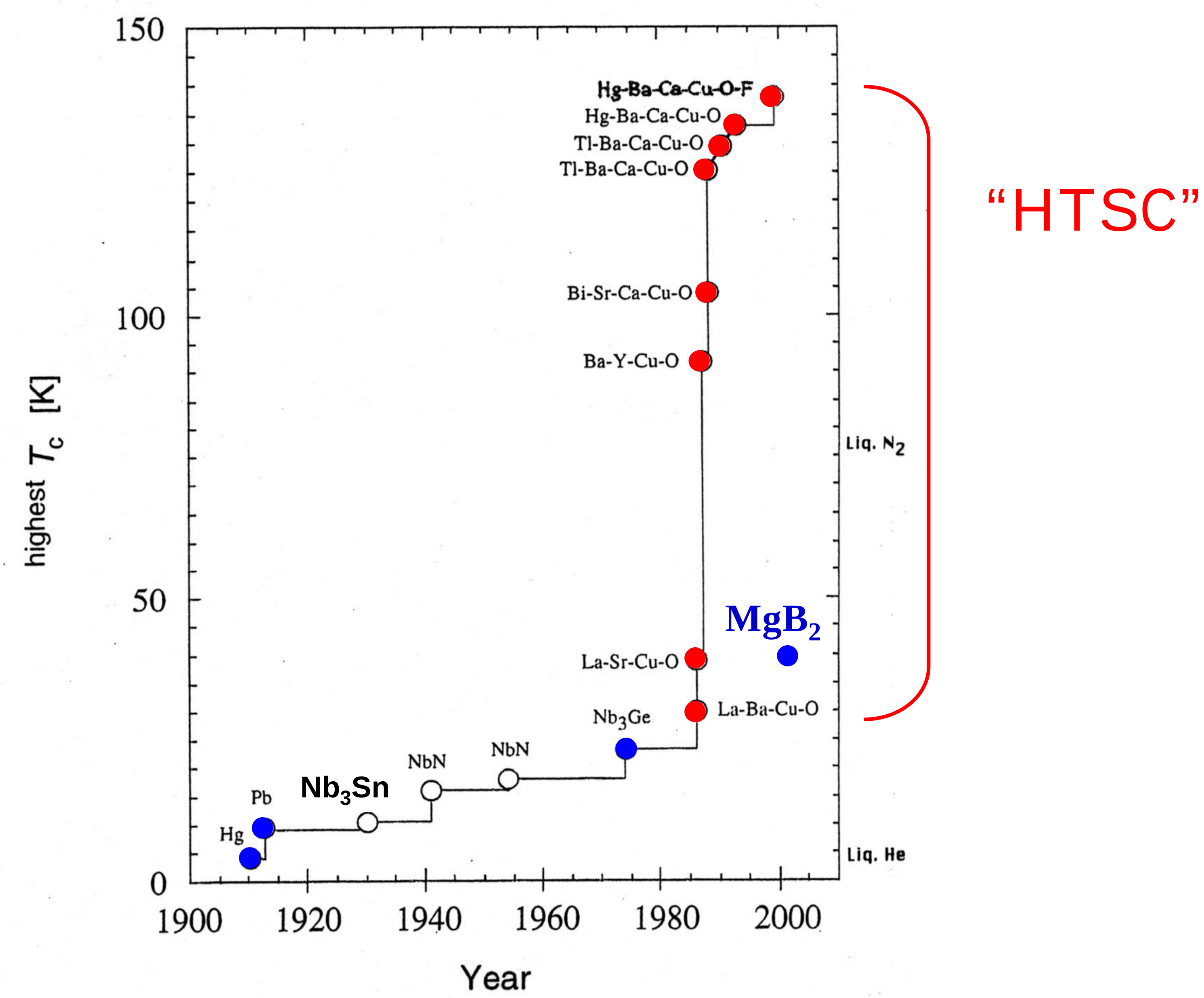

The Meissner Effect
Magnet
Superconductor
Liquid Nitrogen
Foam Container


Type I superconductor
Type II superconductor
$-\mu M$
Superconducting state
Mixed state
Normal state
H_{c1}
H_c
H_{c2}
H

Super-Maglev Train

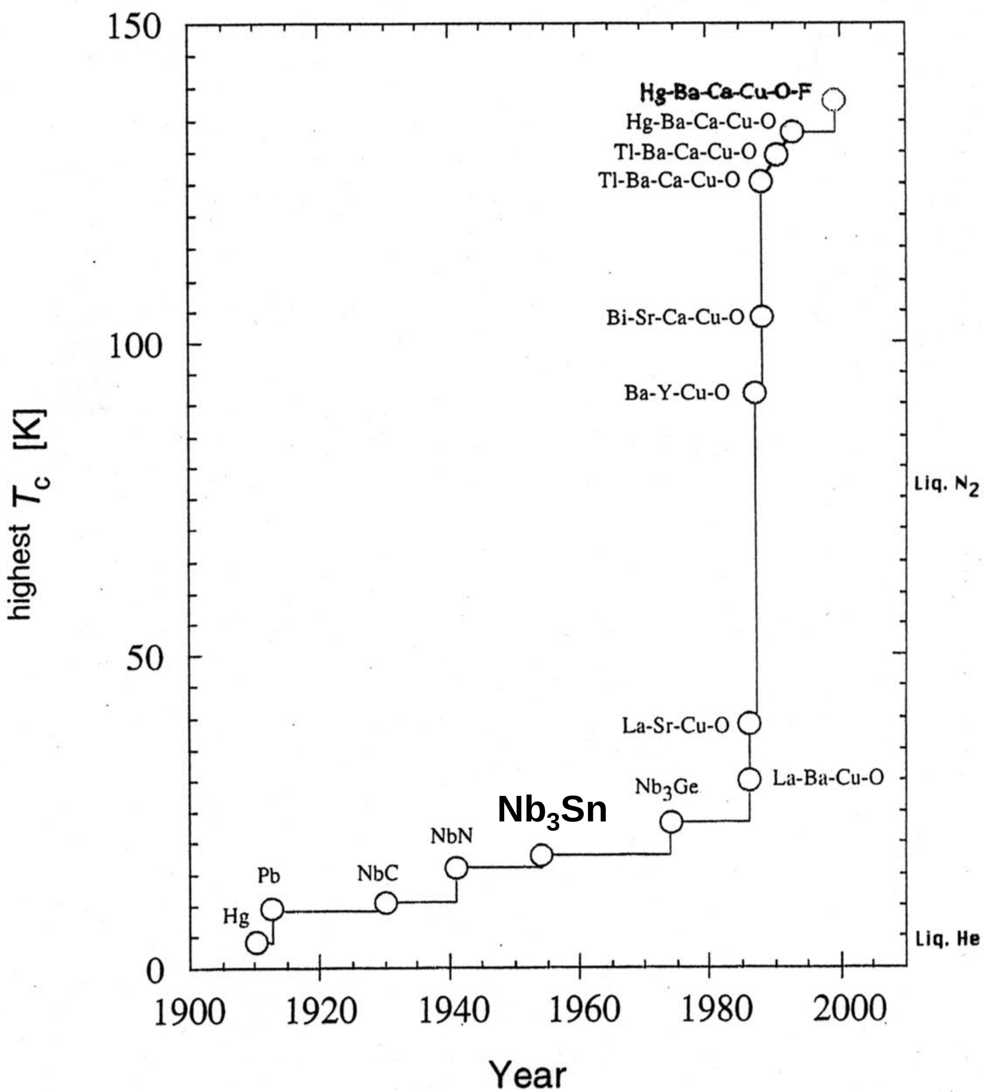
- 603 km / hour
- Test line 42.8 km


Superconducting Elements
In Bulk at Ambient Pressure
At High Pressure
In Modified Form
1
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



150
100
50
0
highest T_c [K]
1900
1920
1940
1960
1980
2000
Year
Hg
Pb
Nb_3Sn
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
MgB_2
Liq. N_2
Liq. He
"HTSC"

Search for new high-T_c superconductors



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

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

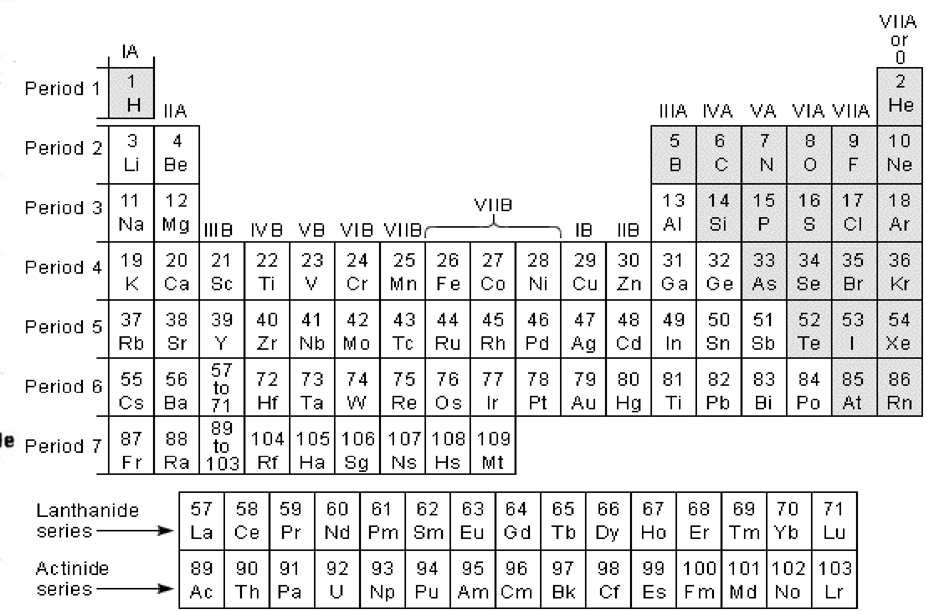
$YBa_2Cu_3O_7$

$Bi_2Sr_2Ca_2Cu_3O_{10}$

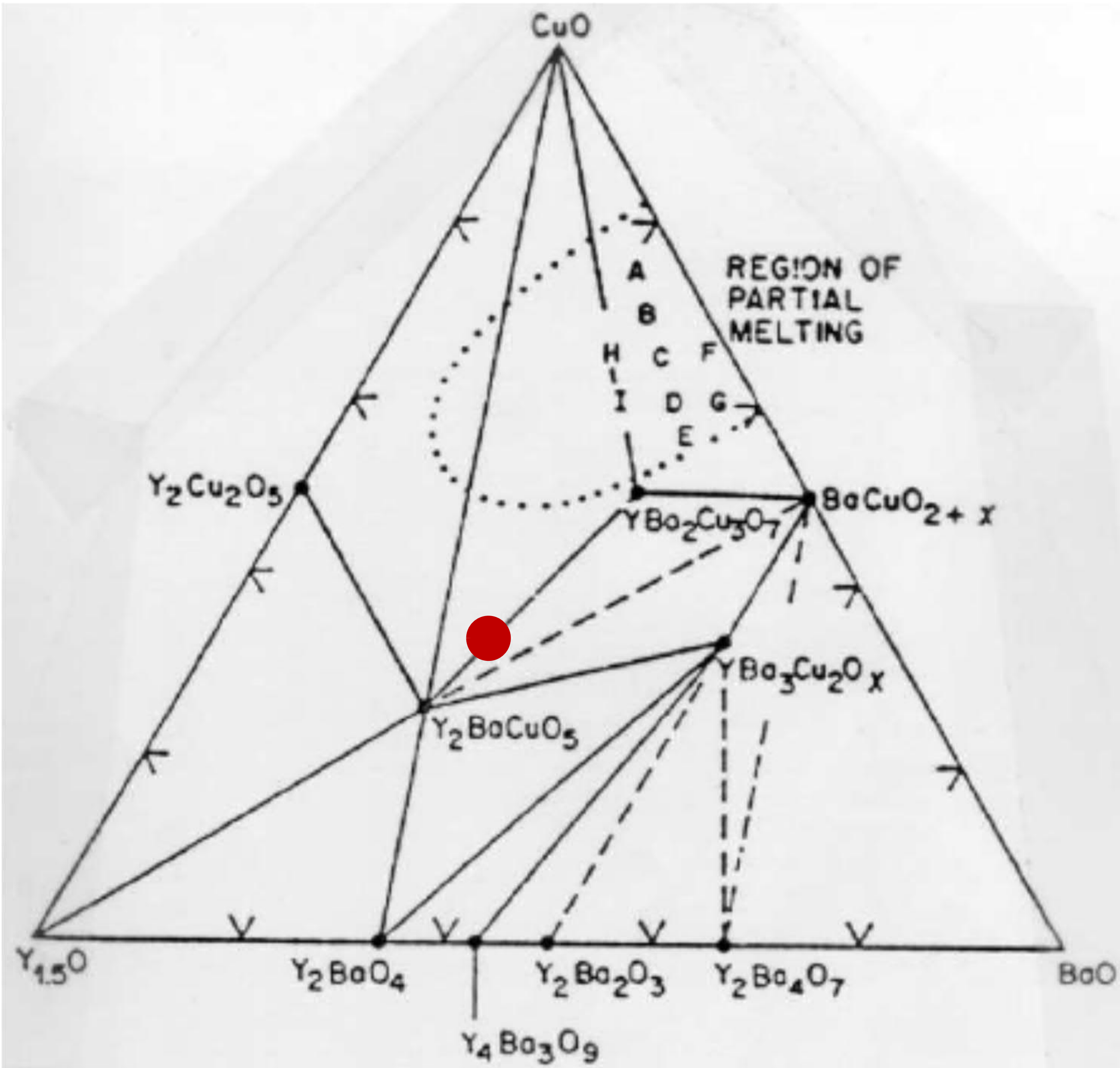
$Tl_2Ba_2Ca_2Cu_3O_{10}$

$TlBa_2Ca_2Cu_3O_9$

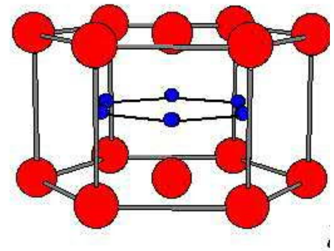
$HgBa_2Ca_2Cu_3O_9$



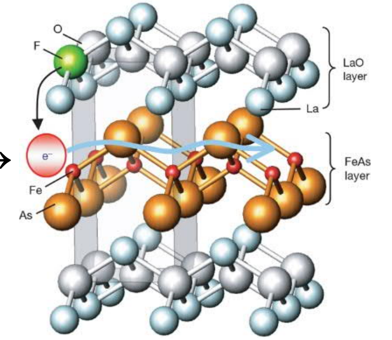
Pseudoternary Y-Ba-Cu-O Phasediagram ($0.5Y_2O_3$-BaO-CuO): 1000 ºC, 1 atm O_2

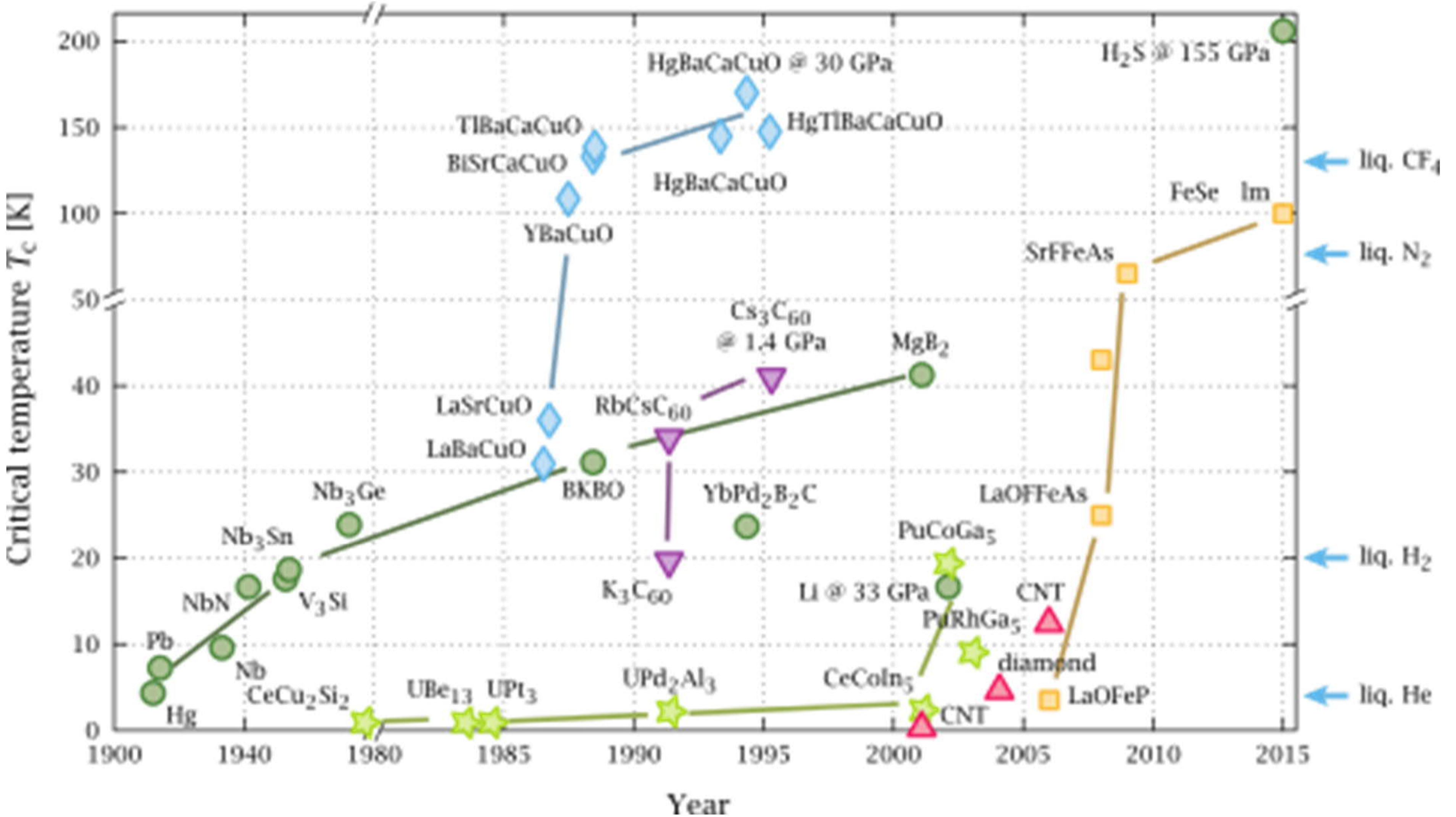


Akimitsu 2001:
MgB_2

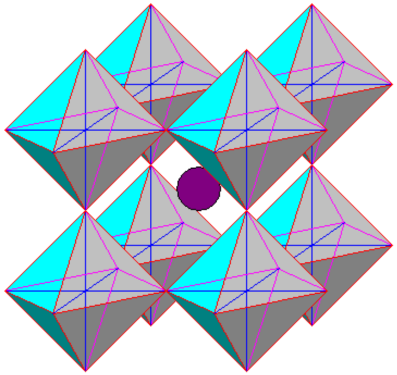


Hosono 2006 → [La(O,F)][FeAs]

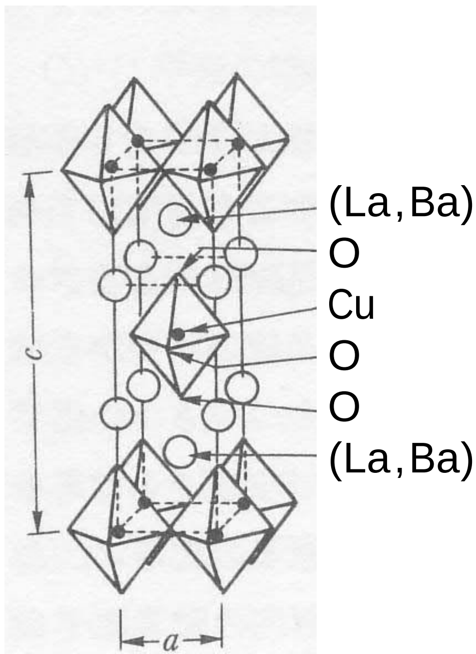


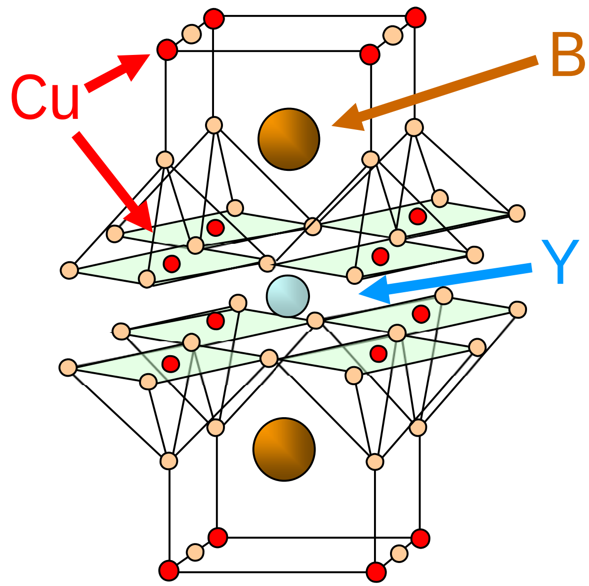


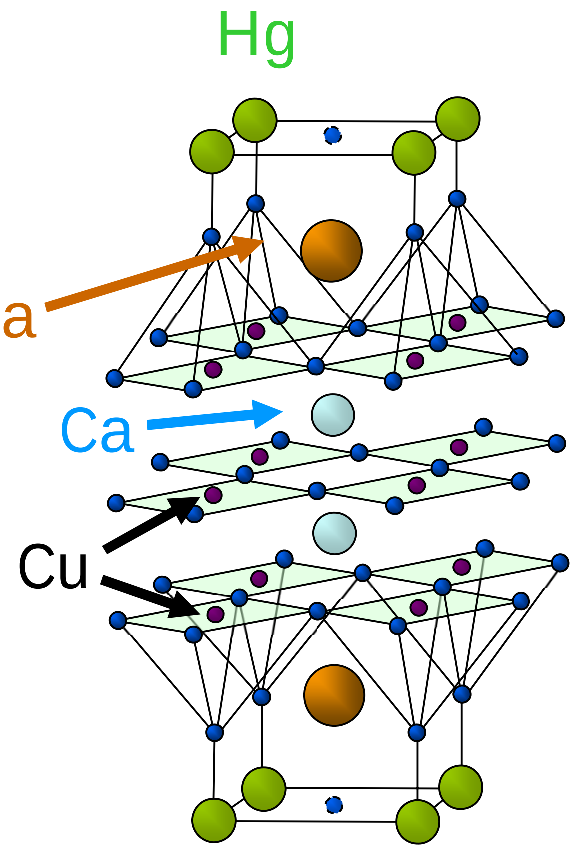
Crystal Structures of High-T_c Superconductive Copper Oxides



Perovskite $CaTiO_3$







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

$T_c \approx 35$ K

$YBa_2Cu_3O_{7-\delta}$

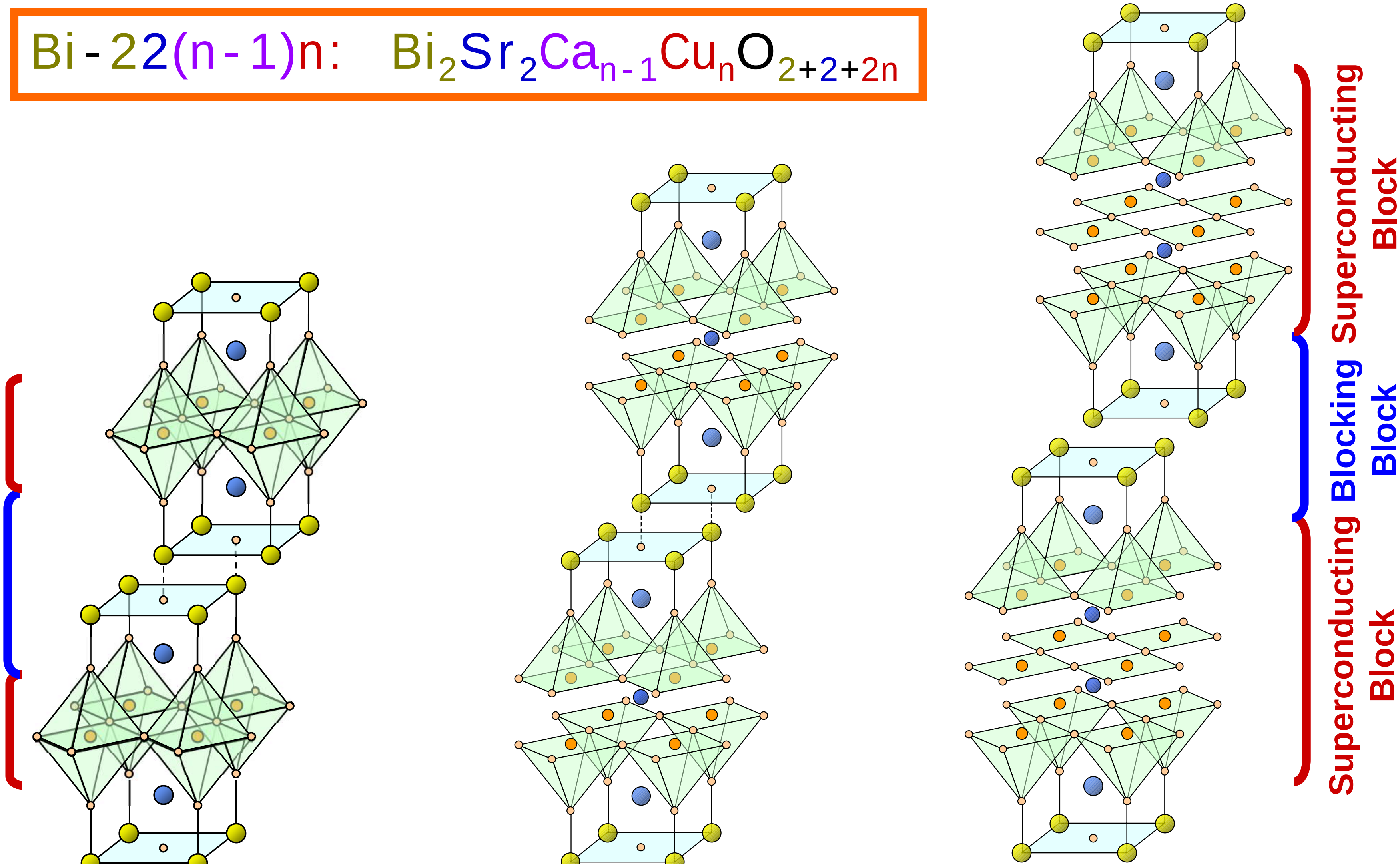
$T_c \approx 92$ K

$HgBa_2Ca_2Cu_3O_{9-\delta}$

$T_c \approx 135$ K

Homologous Series of Superconducting Copper Oxides

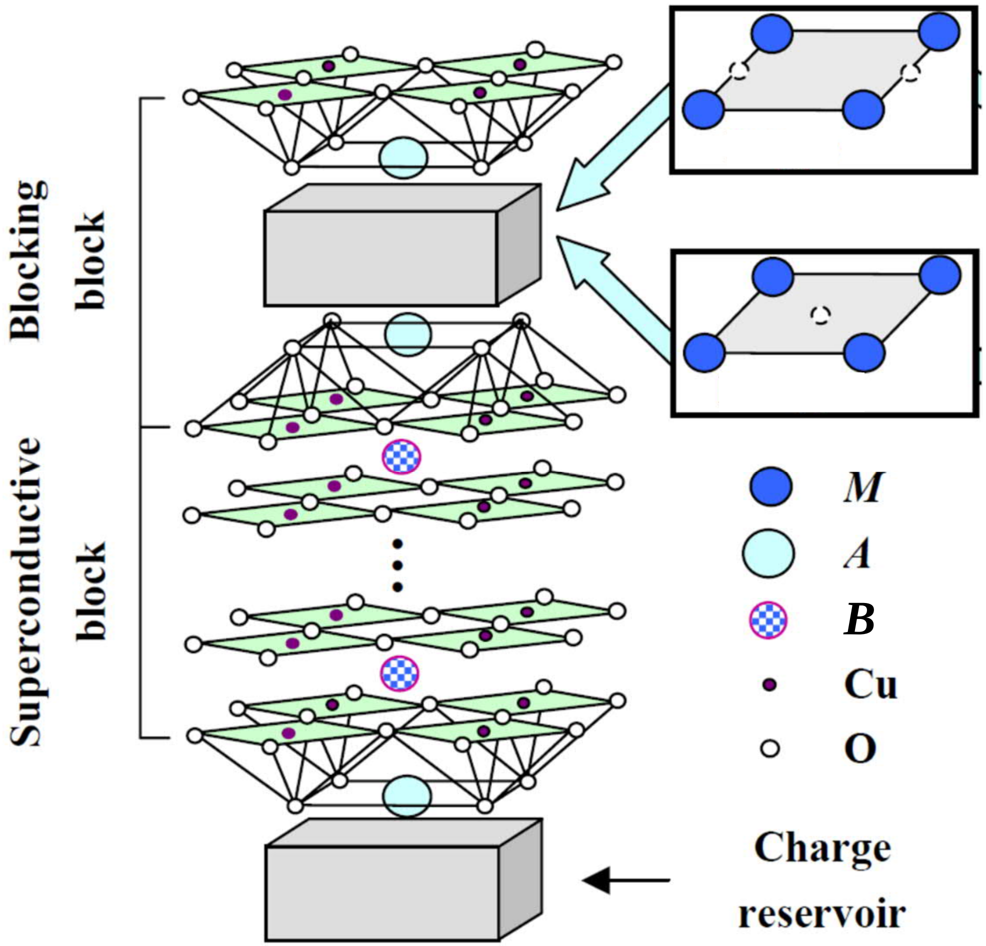
Bi-22(n-1)n: $Bi_2Sr_2Ca_{n-1}Cu_nO_{2+2+2n}$



$Bi_2Sr_2CuO_{6+\delta}$	$Bi_2Sr_2CaCu_2O_{8+\delta}$	$Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$
Bi-2201; $T_c \approx 20$ K	Bi-2212; $T_c \approx 80$ K	Bi-2223; $T_c \approx 110$ K

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

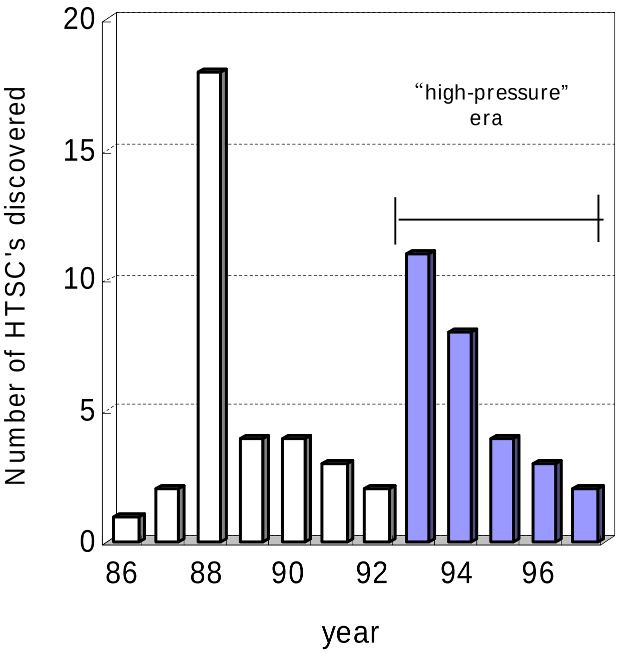


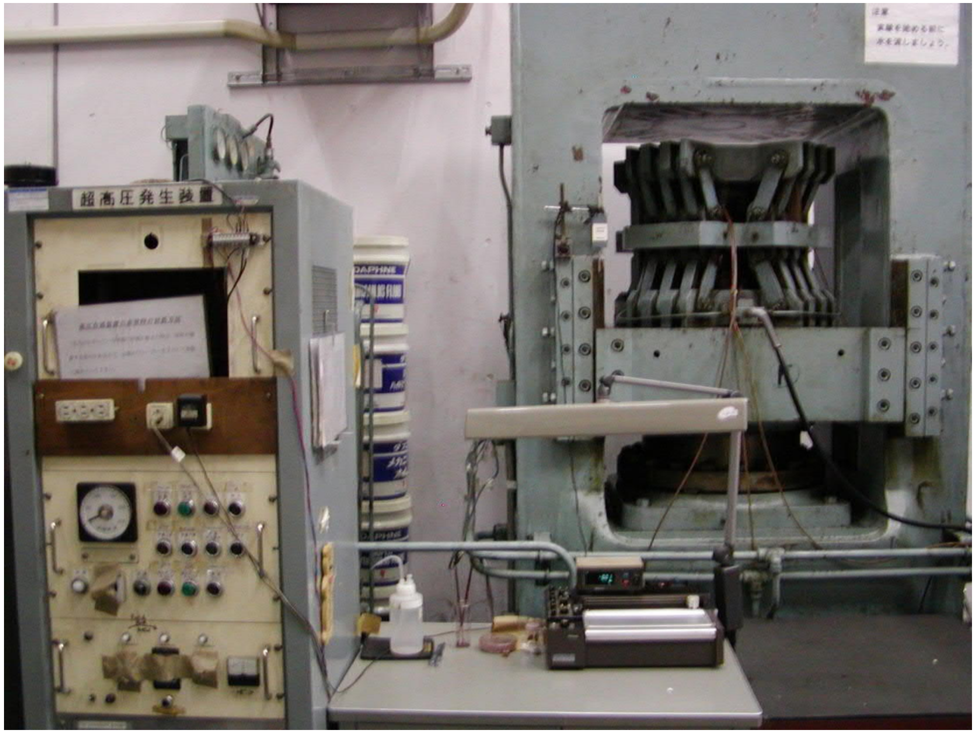
m x $MO_{1\pm\delta}$ layers

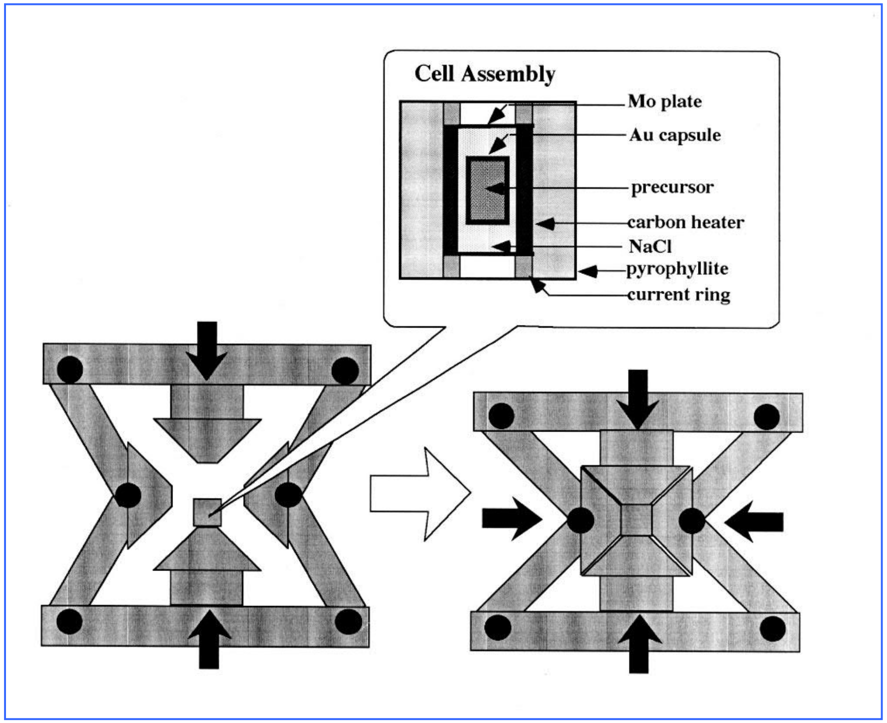
M. Karppinen & H. Yamauchi,
Control of the charge inhomogeneity and high-T_c superconducting properties in homologous series of multi-layered copper oxides,
Mater. Sci. Eng. R **26**, 51-96 (1999).

Ultra-High-Pressure Synthesis

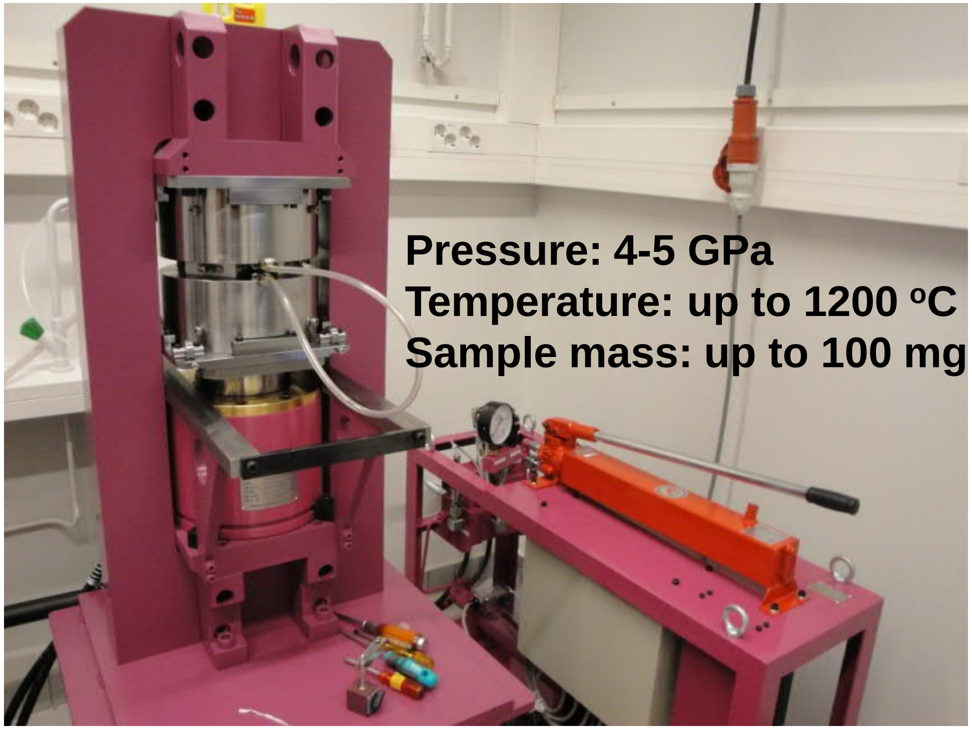
pressure: 2 ~ 8 GPa
sample: 50 ~ 300 mg

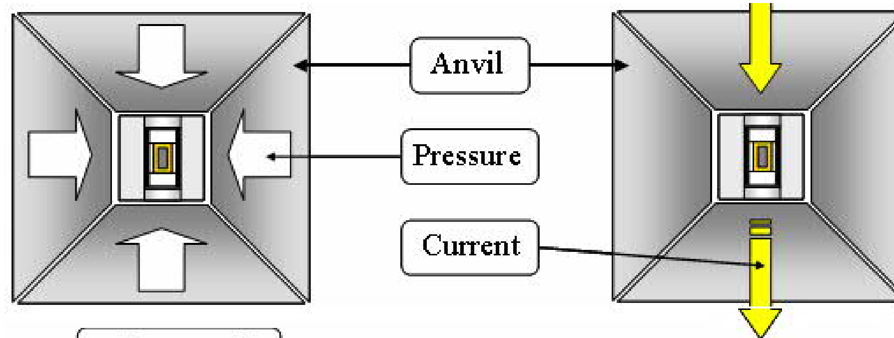


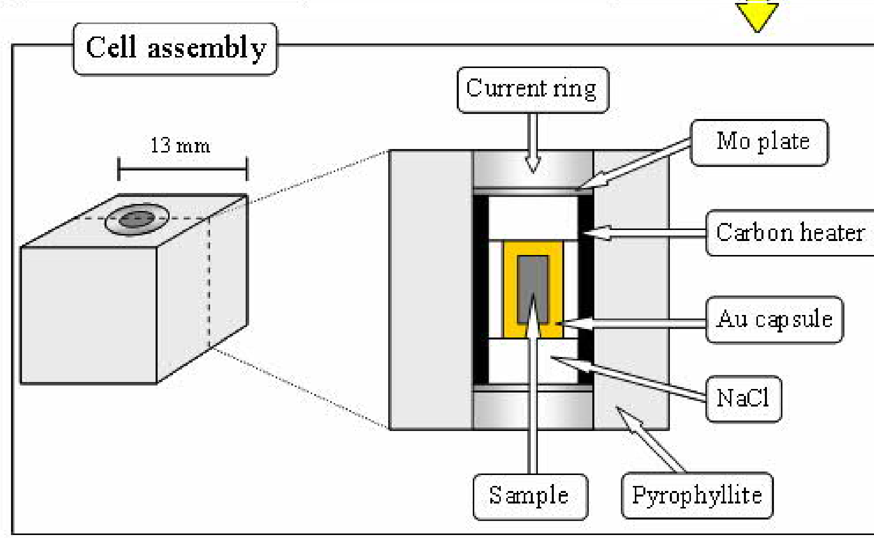


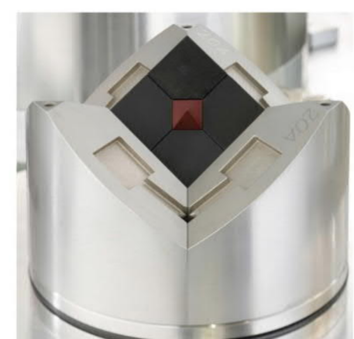


OUR HIGH-PRESSURE EQUIPMENT









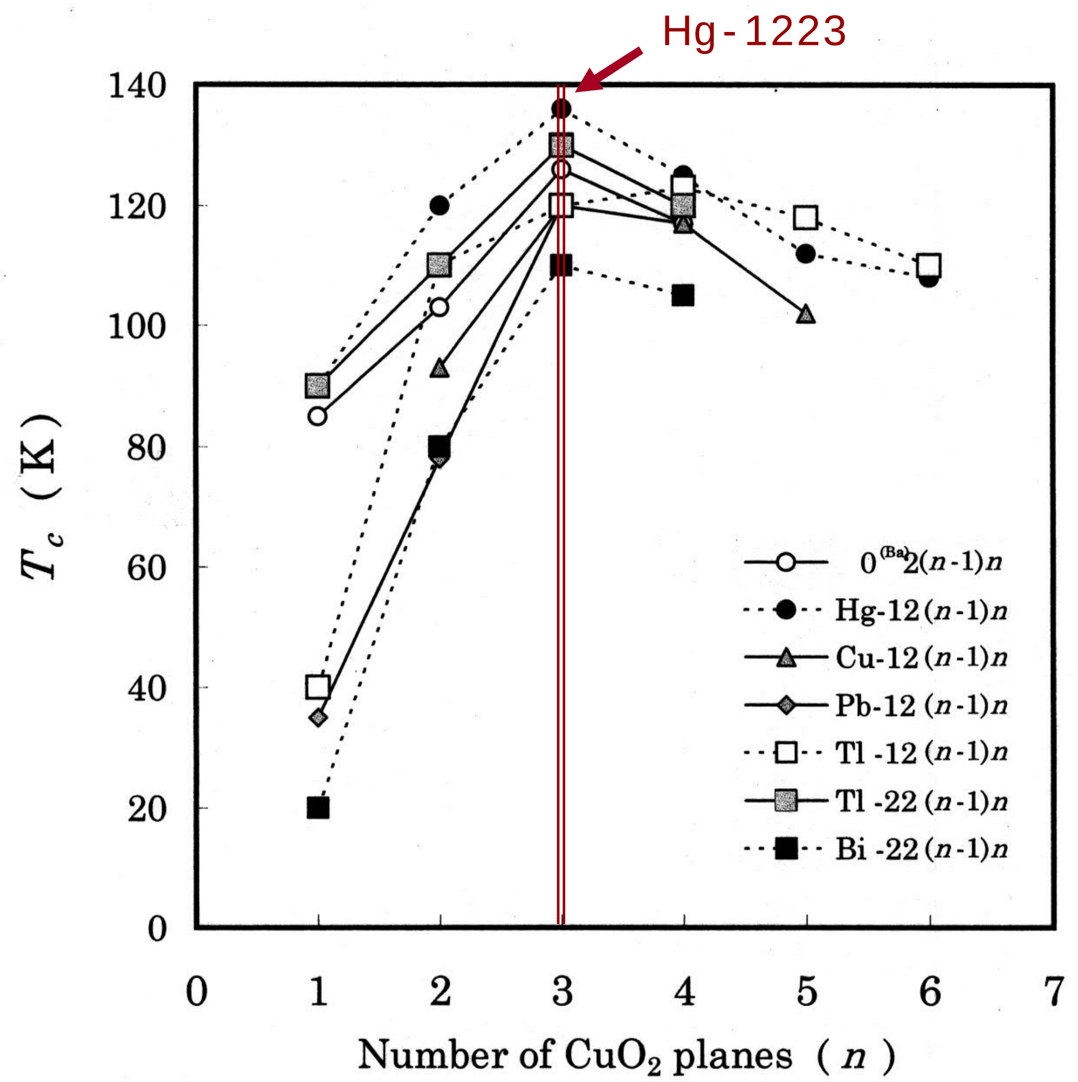
$$M_mA_2Q_{n-1}Cu_nO_{m+2+2n+\delta}$$

M-m2(n-1)n

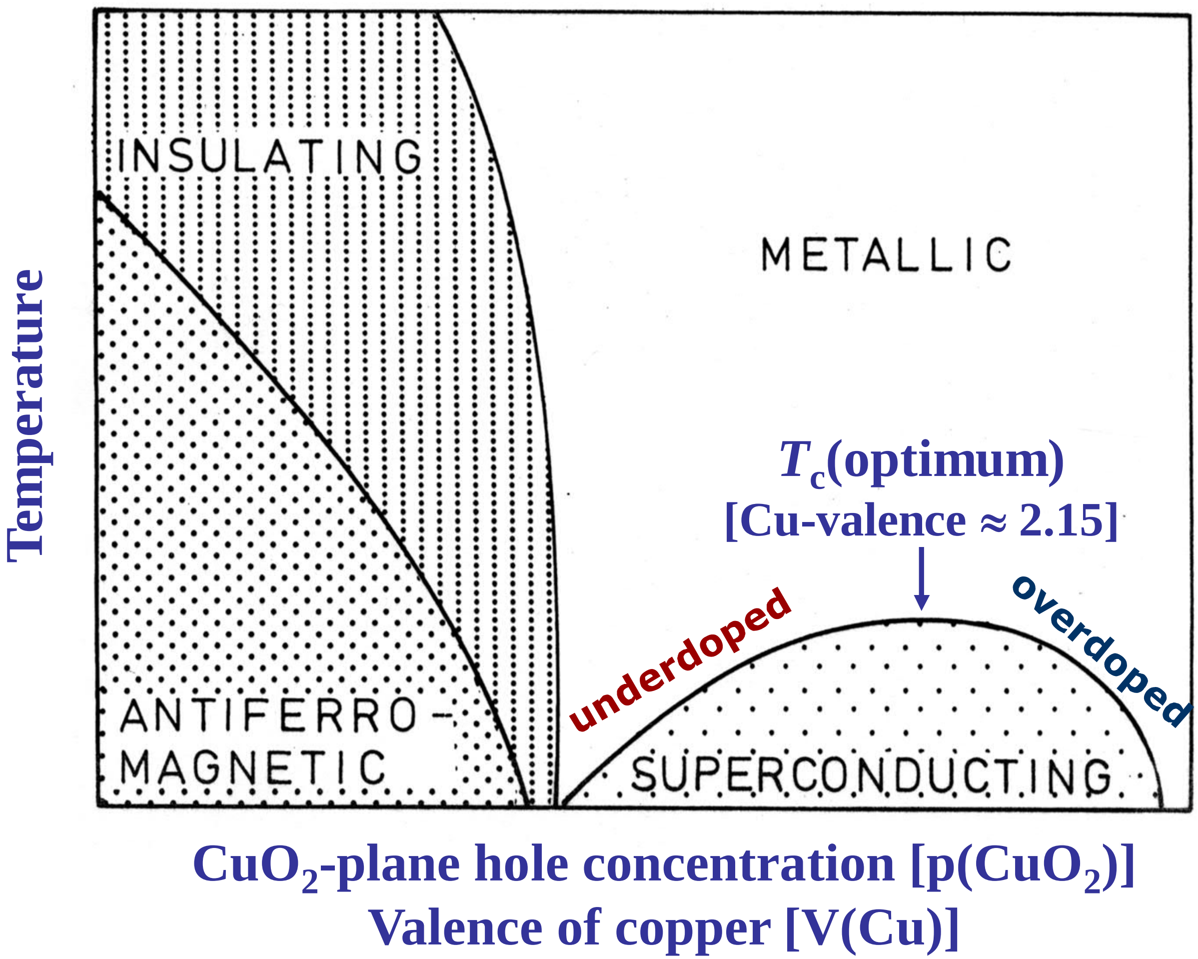
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 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 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

T_c *versus* "number of consecutively stacked CuO_2 planes"



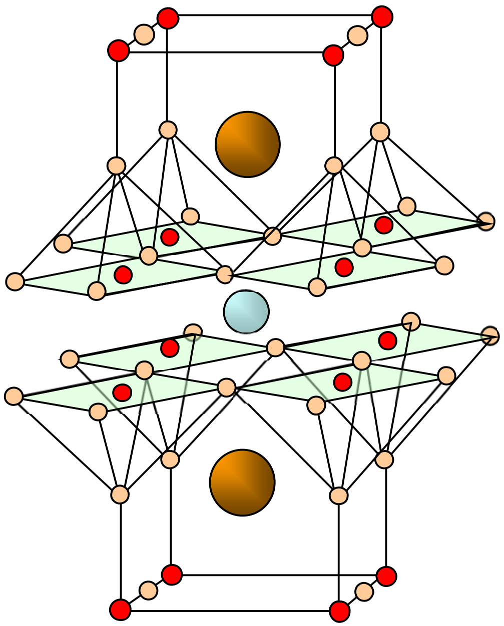
Phase Diagram of HTSC

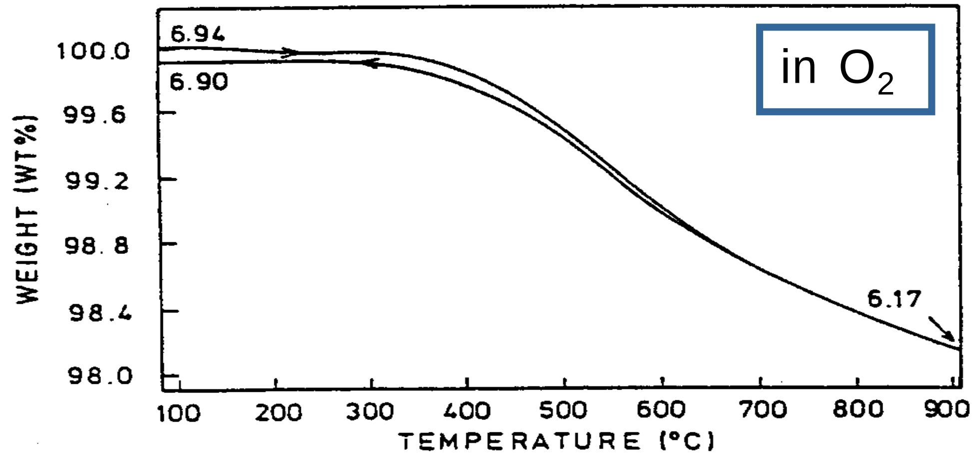


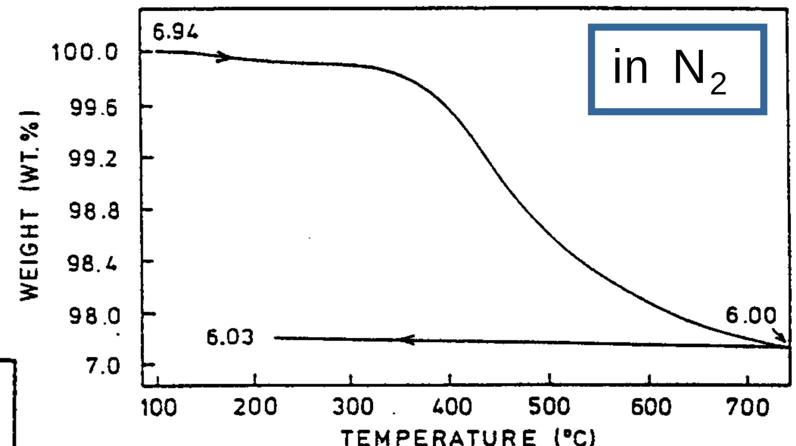
Chemistry

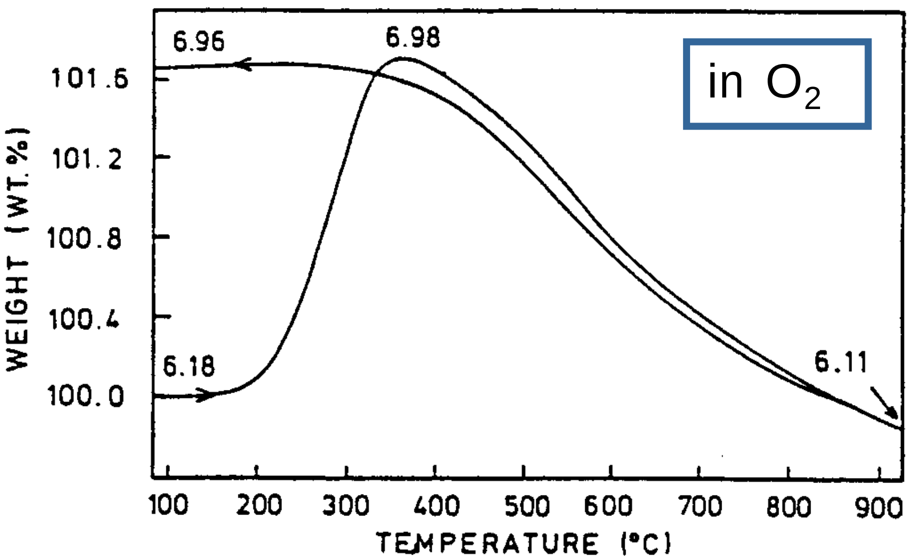
Hole-carrier concentration
p(CuO_2) = V(Cu)-2

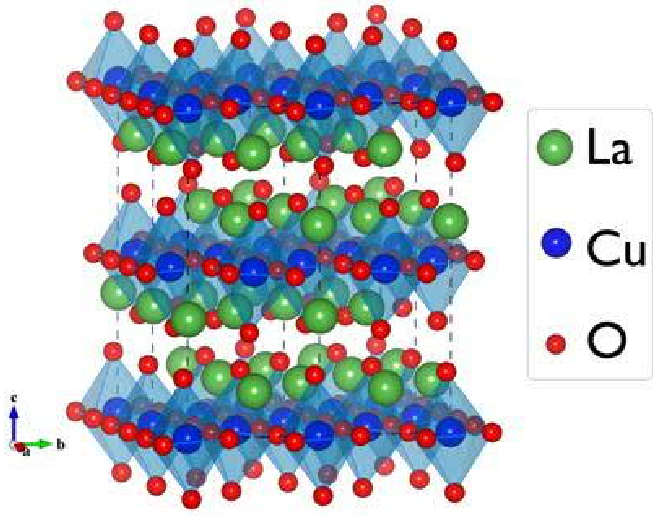
$CuBa_2YCu_2O_{7-\delta}$





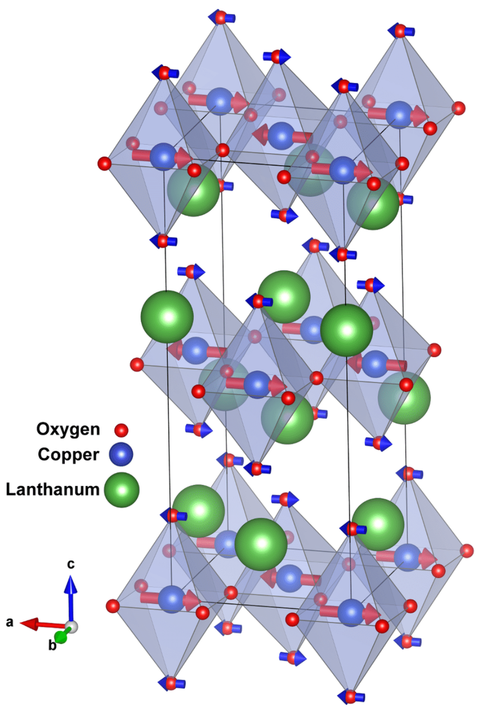


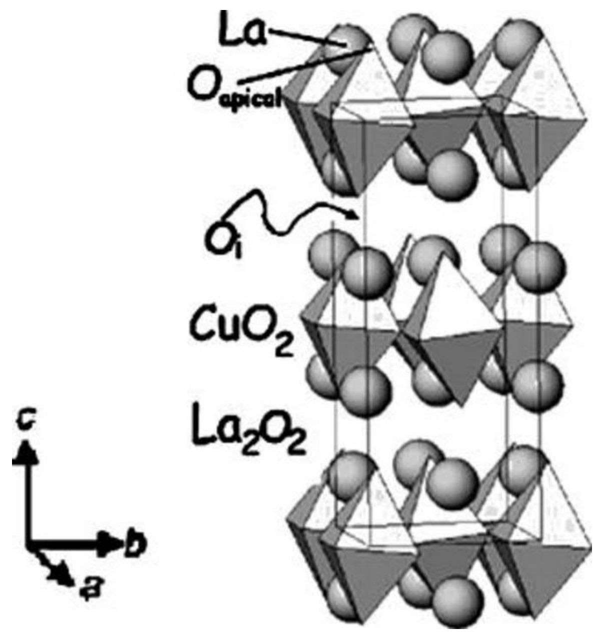


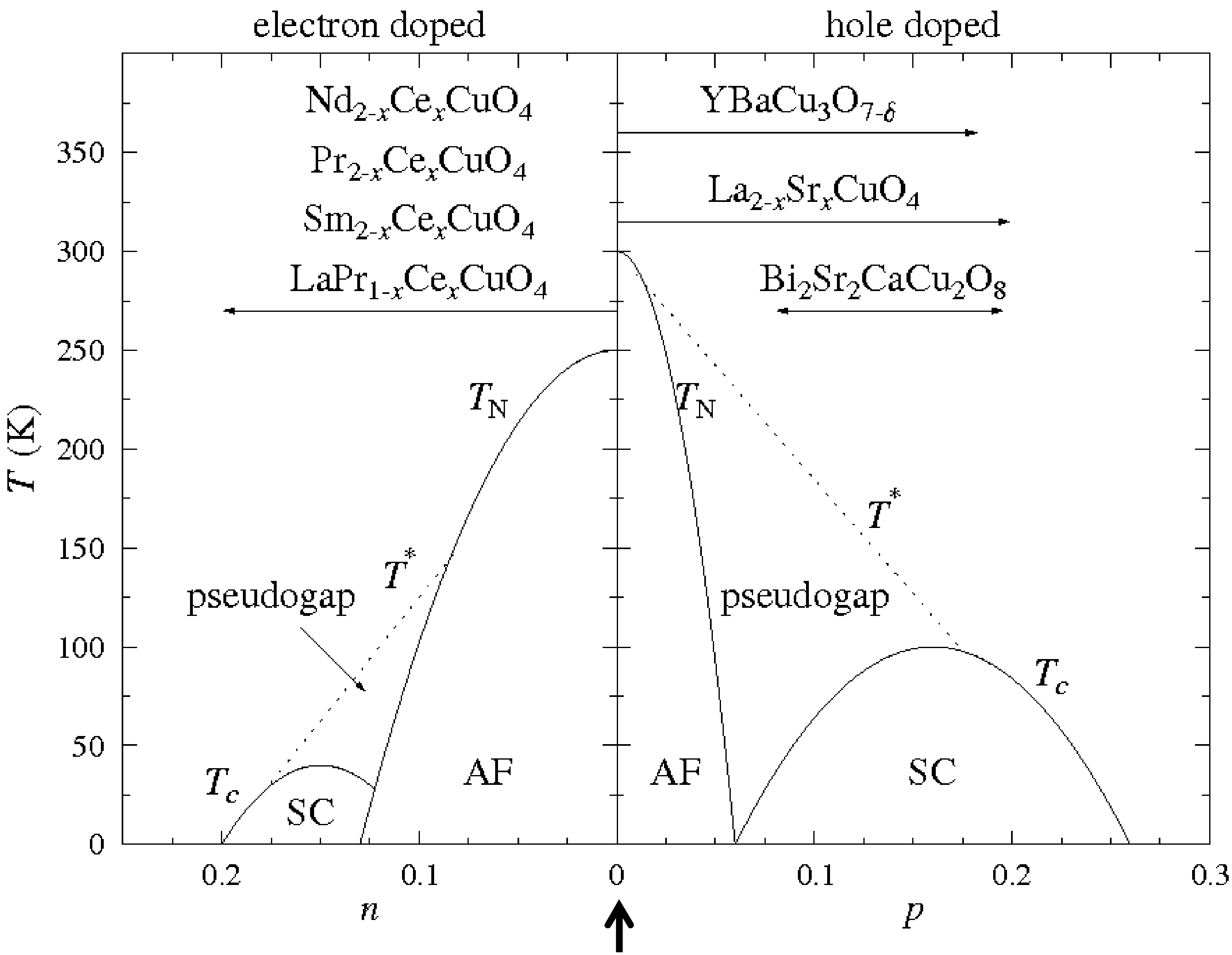


La_2CuO_4

- Is this compound superconducting
- How to increase hole concentration
- What is its M-m2(n-1)n type name
- Does it belong to any general structure





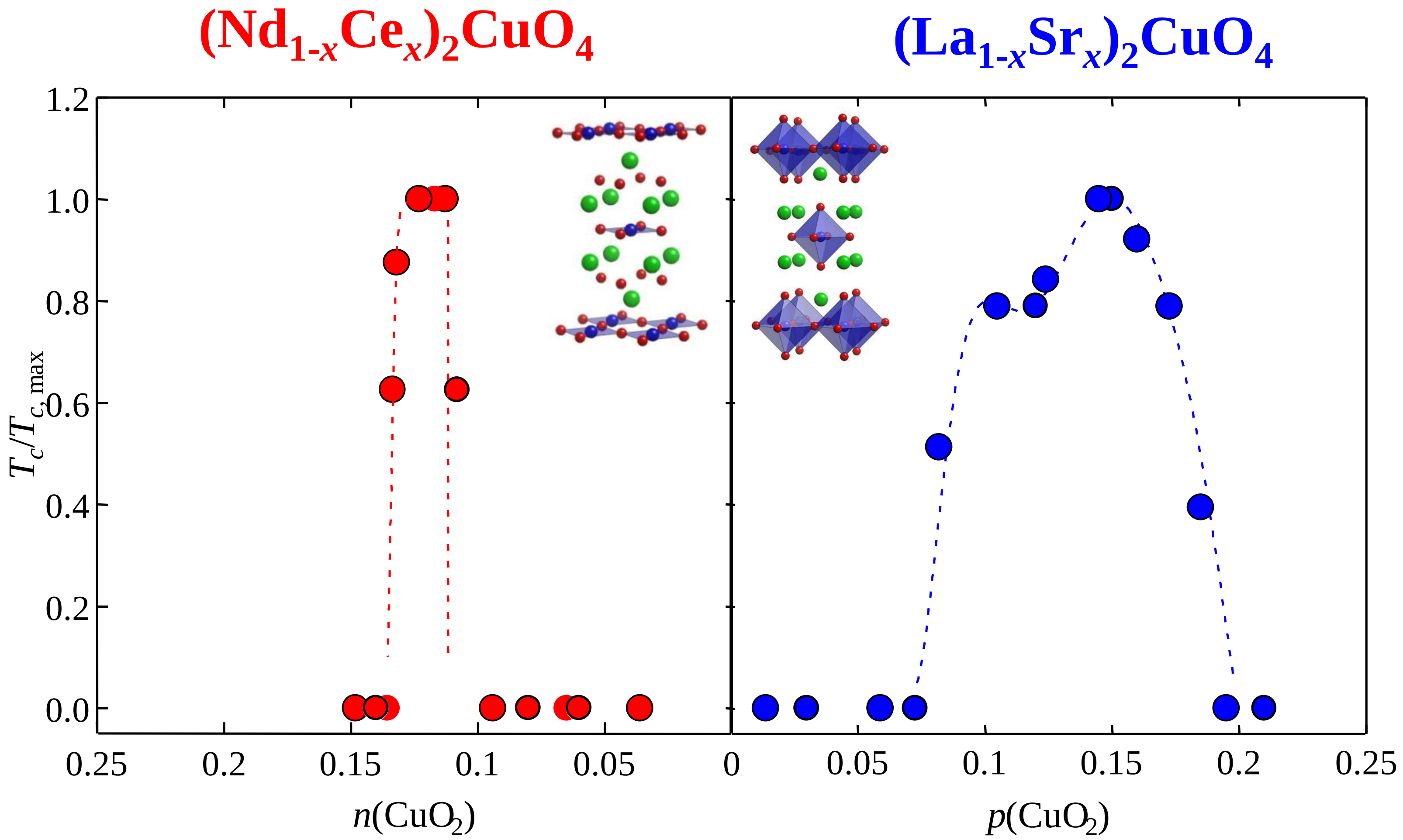


n = electron density = 2 - V(Cu)

V(Cu) = 2

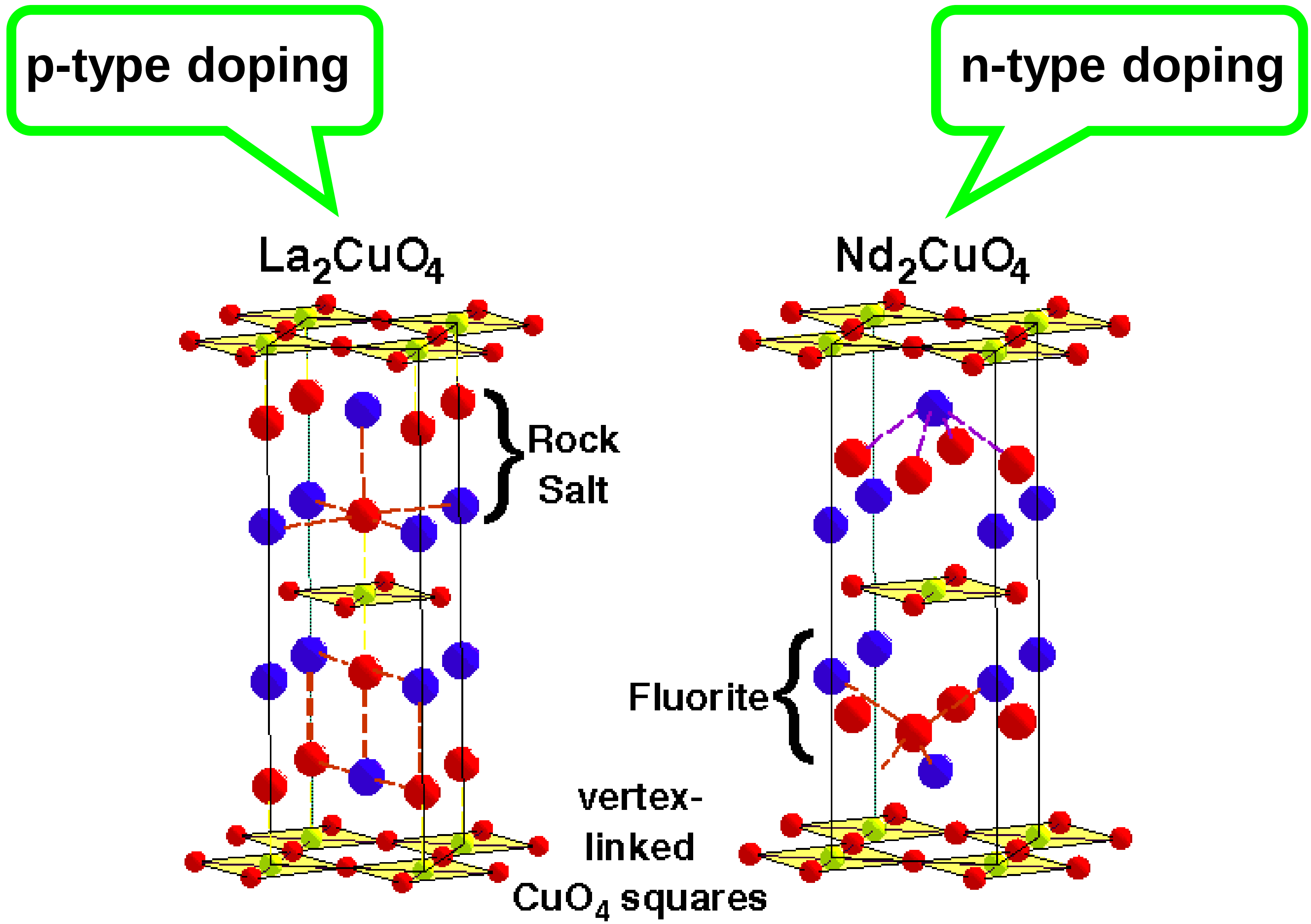
p = hole density = V(Cu) - 2

Superconductivity phase diagrams, *n*-type *vs.* *p*-type



$n(CuO_2) \equiv 2 - V(Cu)$

$p(CuO_2) \equiv V(Cu) - 2$


p-type doping
n-type doping
La_2CuO_4
Nd_2CuO_4
Rock Salt
Fluorite
vertex-linked CuO_4 squares