Functional Inorganic Materials
Fall 2022

Tuesdays: 12.15 - 14.00 (U8)
Thursdays: 10.15 - 12.00 (Ke1)

#	Date	Who	Topic
1	Mon 5.9.	Maarit	Introduction + Materials design consepts
2	Thu 8.9.	Antti	Introduction + Computational materials design
3	**Tue 13.9.**	**Maarit**	**Superconductivity: High-T_c superconducting Cu oxides**
4	Thu 15.9.	Maarit	Magnetic oxides
5	Tue 20.9.	Maarit	Ionic conductivity (Oxygen): Oxygen storage and SOFC
6	Thu 22.9.	Maarit	Ionic conductivity (Lithium): Li-ion battery
7	Tue 27.9.	Antti	Thermal conductivity
8	Thu 29.9.	Antti	Thermoelectricity
9	Tue 4.10.	Antti	Piezoelectricity
10	Thu 6.10.	Antti	Pyroelectricity and ferroelectricity
11	Tue 11.10.	Maarit	Hybrid materials
12	Thu 13.10.	Antti	Luminescent and optically active materials

LECTURE 3: (High-T_c) Superconductivity

- Zero resistance, Meissner effect, Cooper pair, Josephson junction
- Type-I and Type-II superconductors
- History & Impact (on material research!) & Applications
- New-material discoveries: Design principles, Intuition & Good luck !
- Relations to Perovskite & Ruddlesden-Popper structures
- Multi-layered crystal structure & Homologous series concept
- 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 $Bi_2Sr_2Ca_2Cu_3O_{10\pm\delta}$

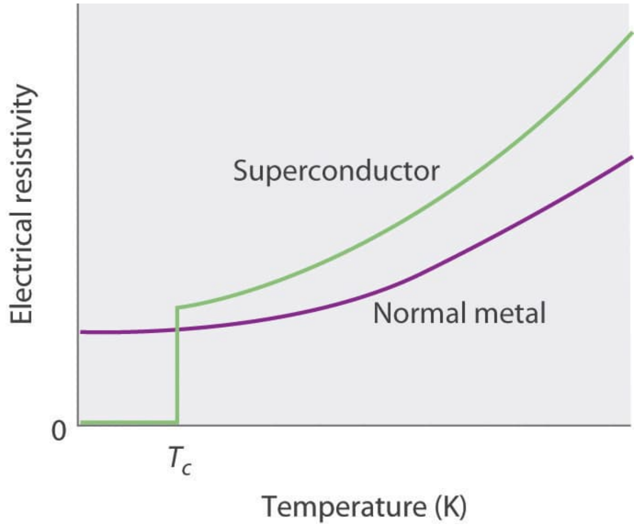
   a) Give the systematic name (= chemical formula abbreviation) for each compound.

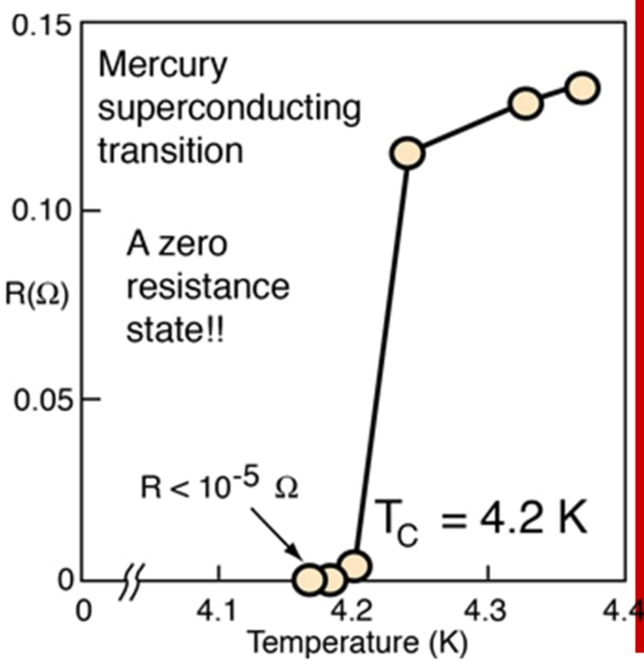
   b) Which of the compounds should have the highest T_c (when optimized); give the reason for your choice!

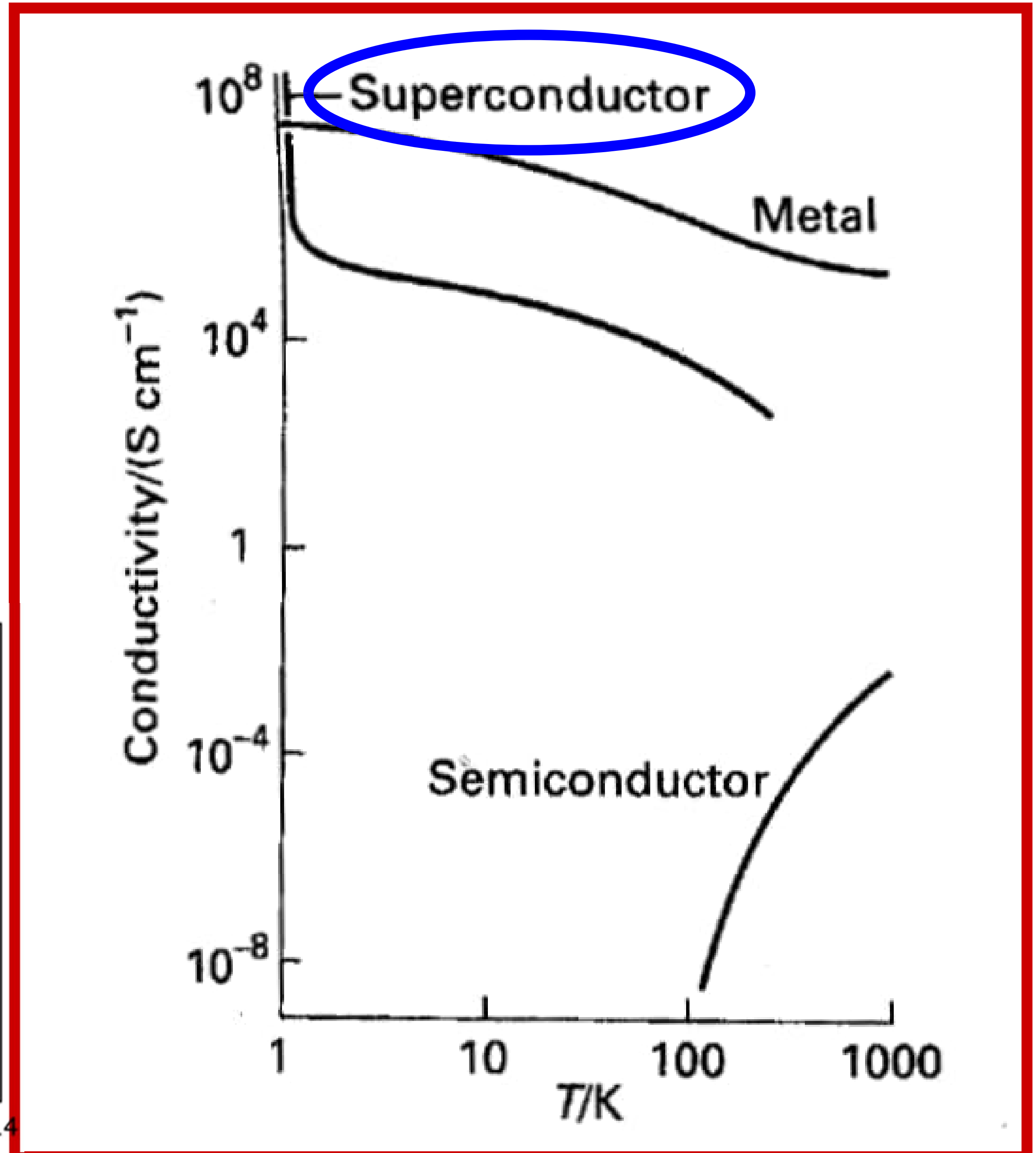
   c) Explain the importance of oxygen nonstoichiometry parameter δ for these compounds.

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

2. Nb_3Sn and Nb_3Ge are important ”low-temperature” superconductors and members of the so-called ”A15 family” of intermetallic compounds. Please write a <u>short</u> essay with approximately 3-5 references to discuss few aspects (e.g. history, superconductivity characteristics, application?) which you find most interesting related to these materials.


Electrical resistivity
Superconductor
Normal metal
0
T_c
Temperature (K)


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


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

SUPERCONDUCTIVITY

Nobel 1913

Superconductivity

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

Meissner effect

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

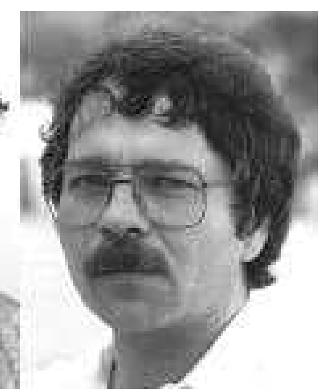
High-T_c superconductivity

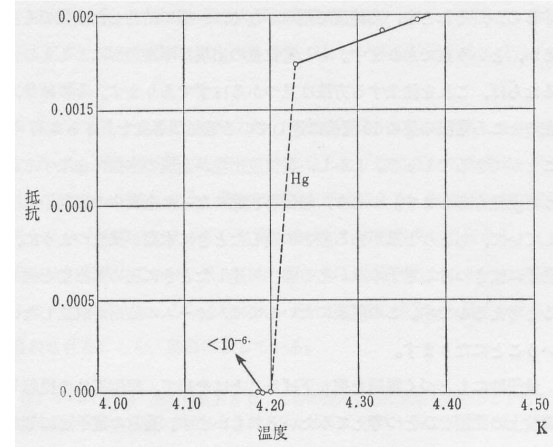
- 1986: Bednorz and Müller
- $(La,Ba)_2CuO_4$ (T_c = 30~40 K)

Present record in T_c:

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

Nobel 1987

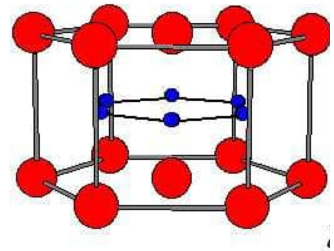




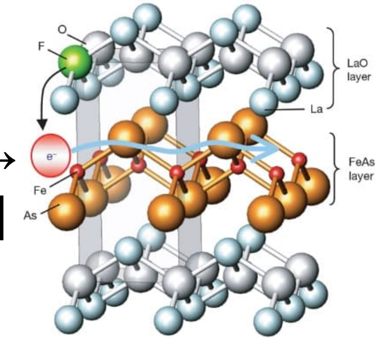
Kamerlingh-Onnes Institute,
@University of Leiden, the Netherlands

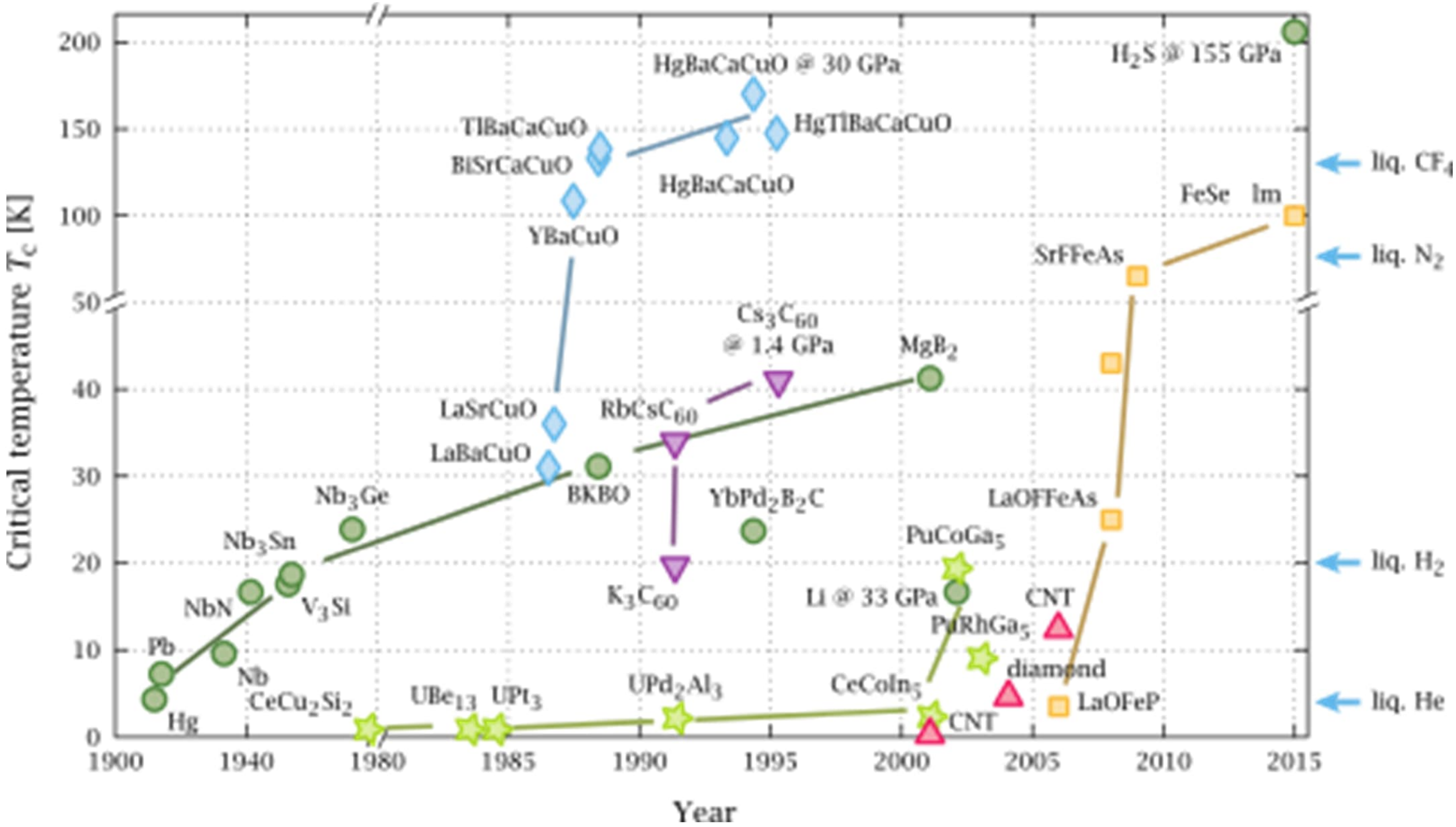
Heike Kamerlingh-Onnes and J.D. van der Waals

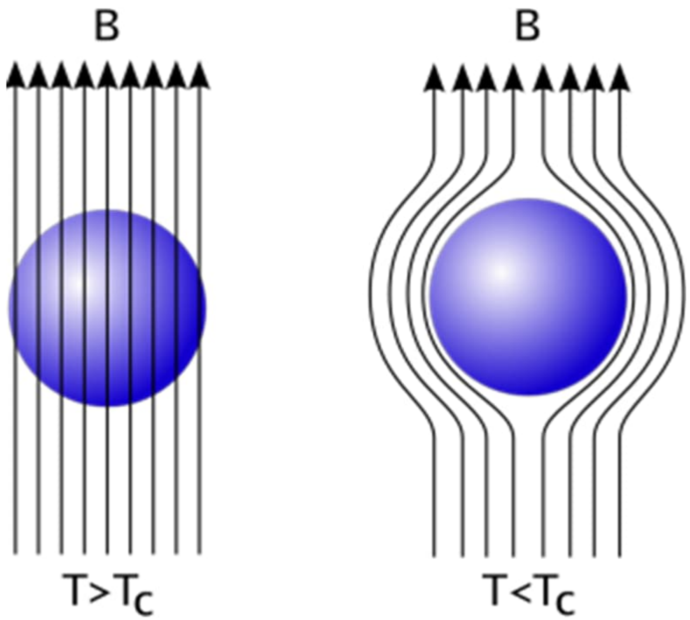
Akimitsu 2001:
MgB_2

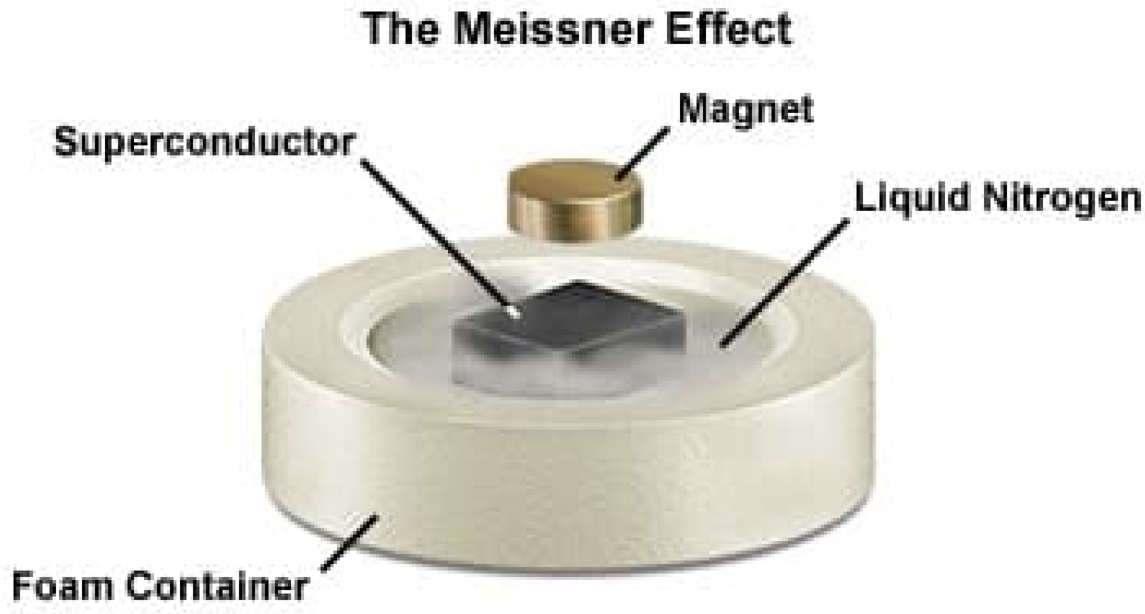


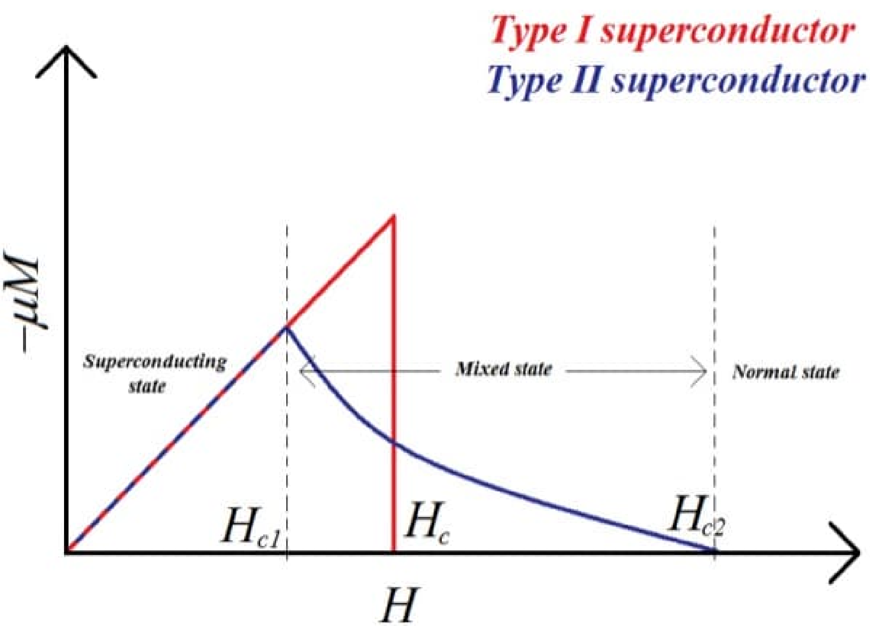
Hosono 2006 →
[La(O,F)][FeAs]











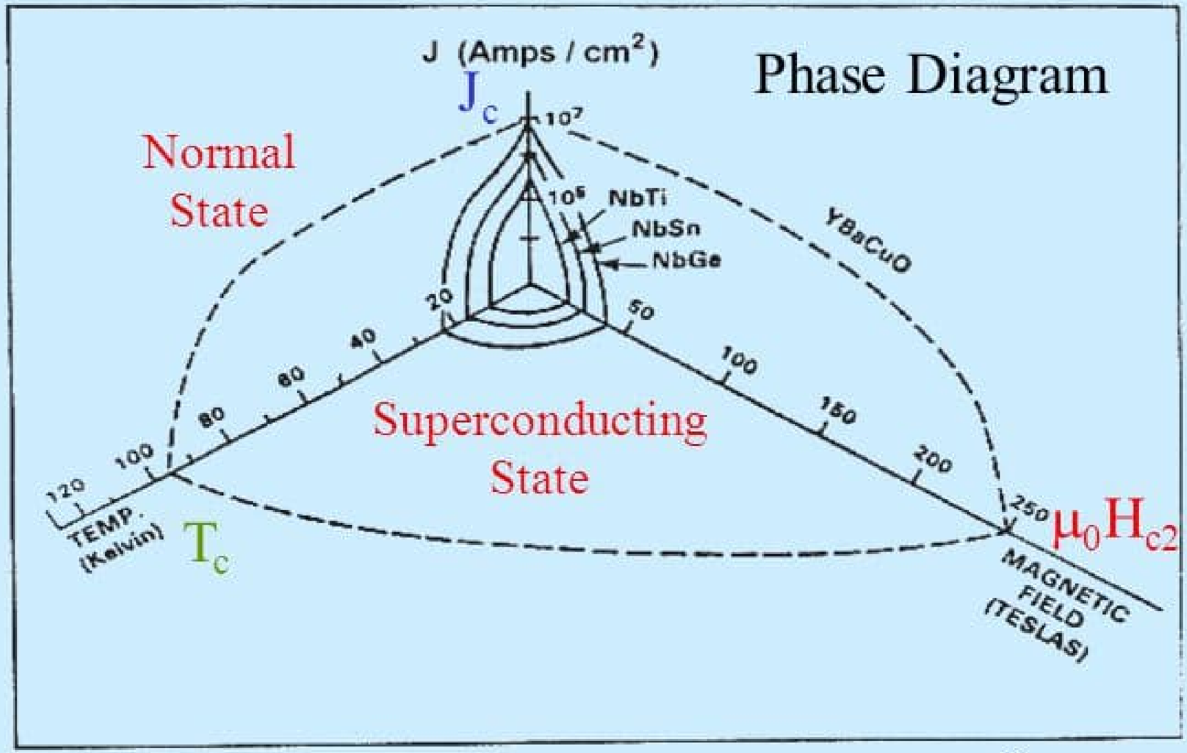
Type-1 Examples:

- Hg, Pb, most of the pure metals

Type-2 Examples:

- Nb, V, NbTi, Nb_3Sn
high-T_c copper oxides

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

Ted Geballe 100 years
Jan. 2020

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.

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.

[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).

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.

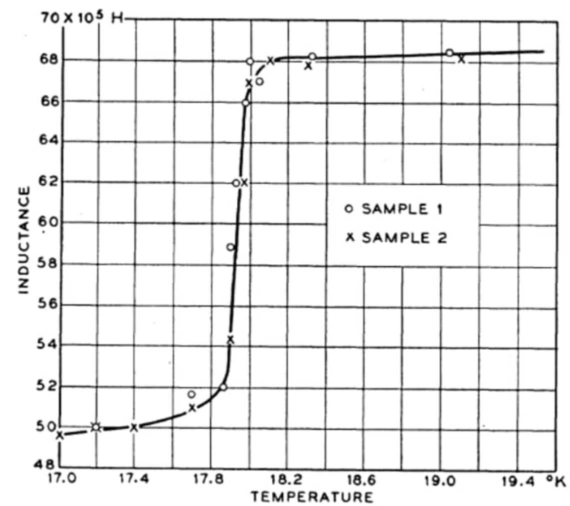
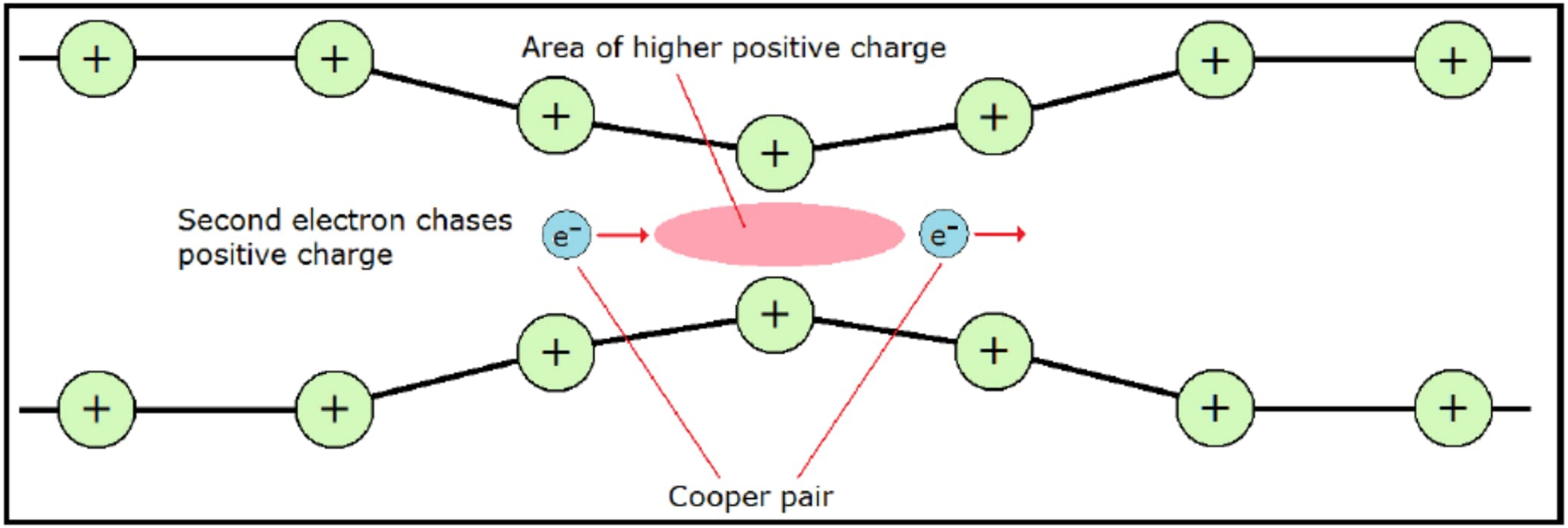


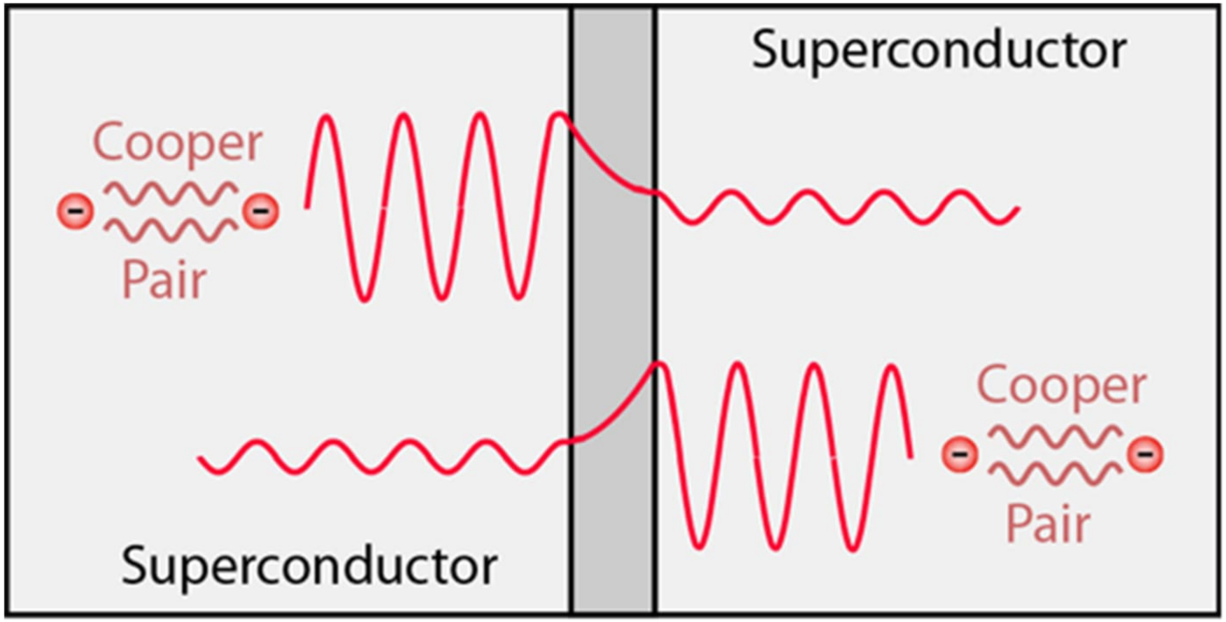
Fig. 1. Variation of susceptibility with temperature of Nb_3Sn.

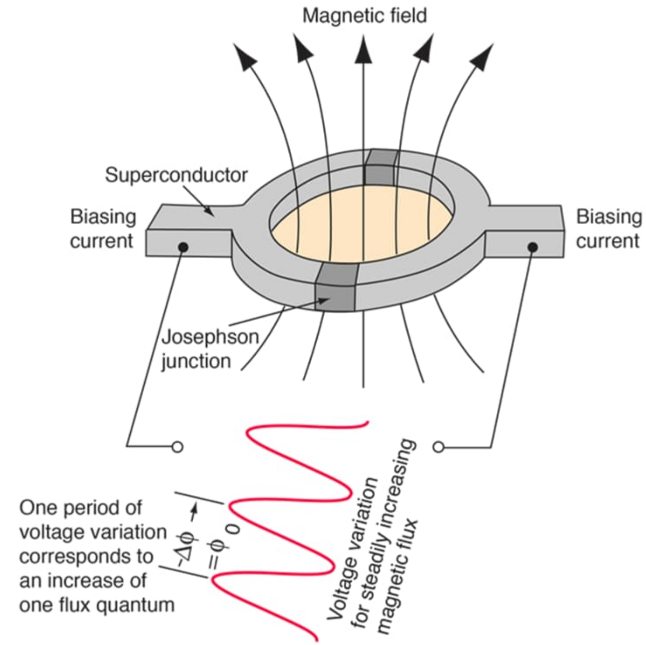
Bardeen, Cooper & Schrieffer

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



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



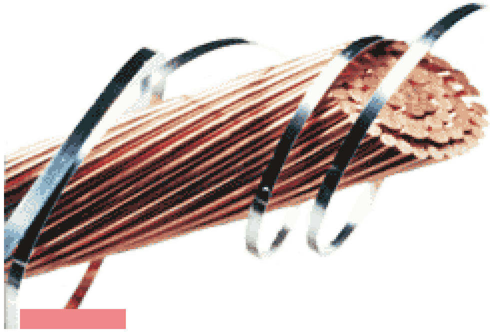


Josephson Junction & SQUID

- 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)**

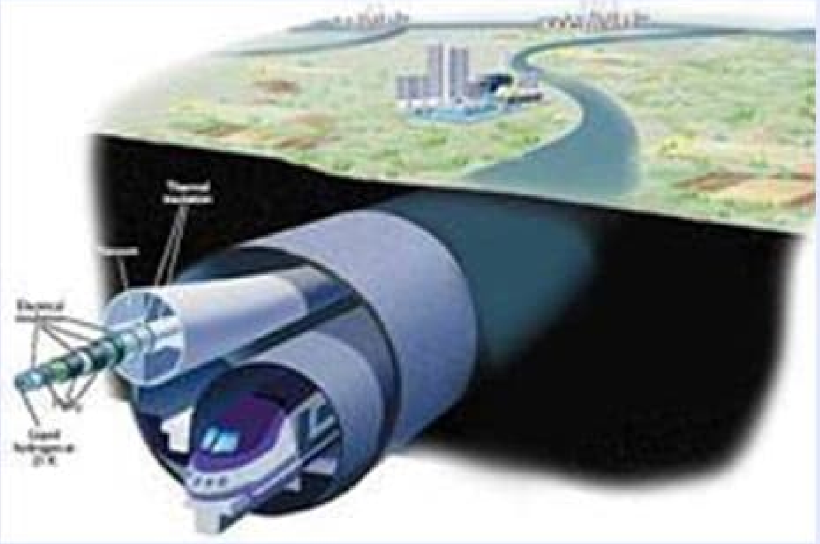
→ **SQUID, NMR, MRI**

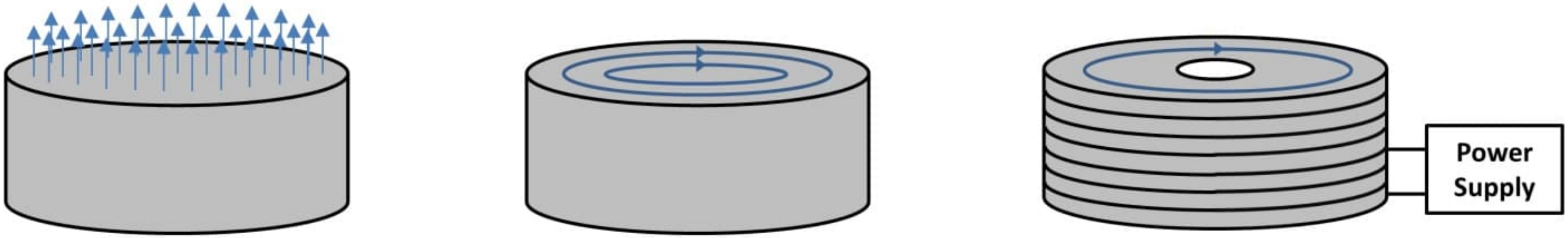
- **Supercomputers (Josephson)**

Applications using Superconductors

Superconducting power transmission

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

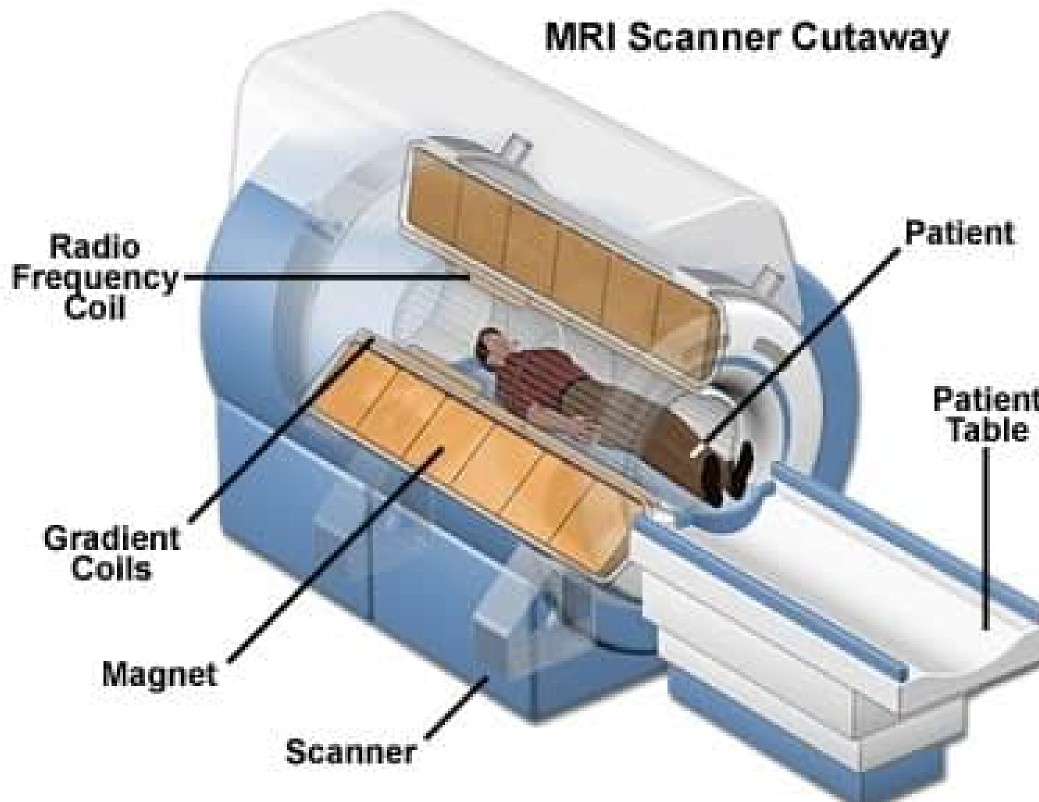




Permanent ferromagnet
Spin
Neodymium N-B-Fe (1.5 T)

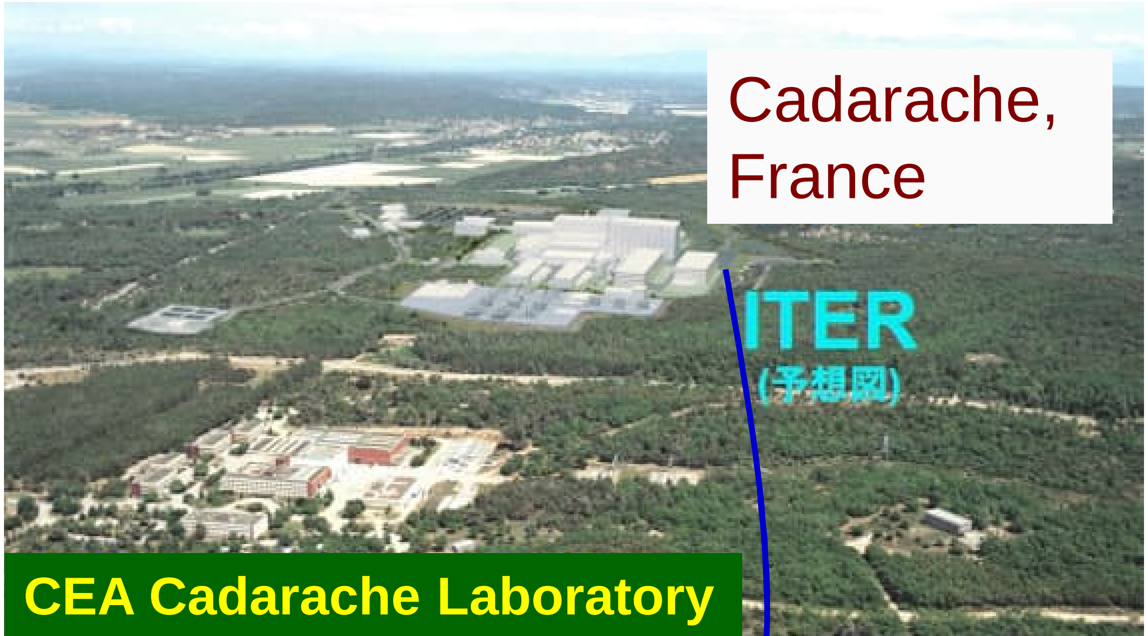
Bulk superconductor
Induced, superconducting loop current
HTS (17 T), MgB_2 (5 T)

Electromagnet
Supplied loop current
Cu (2 T), HTS (> 30 T)



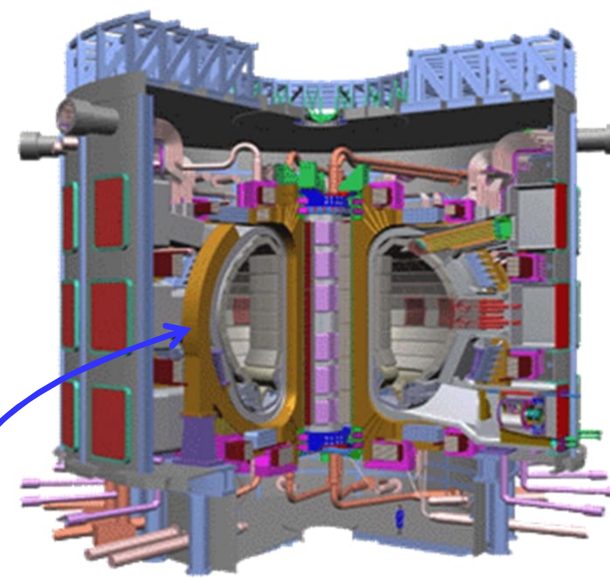
ITER: International Thermonuclear Experimental Reactor

since October, 2007



Nuclear Fusion Reactor

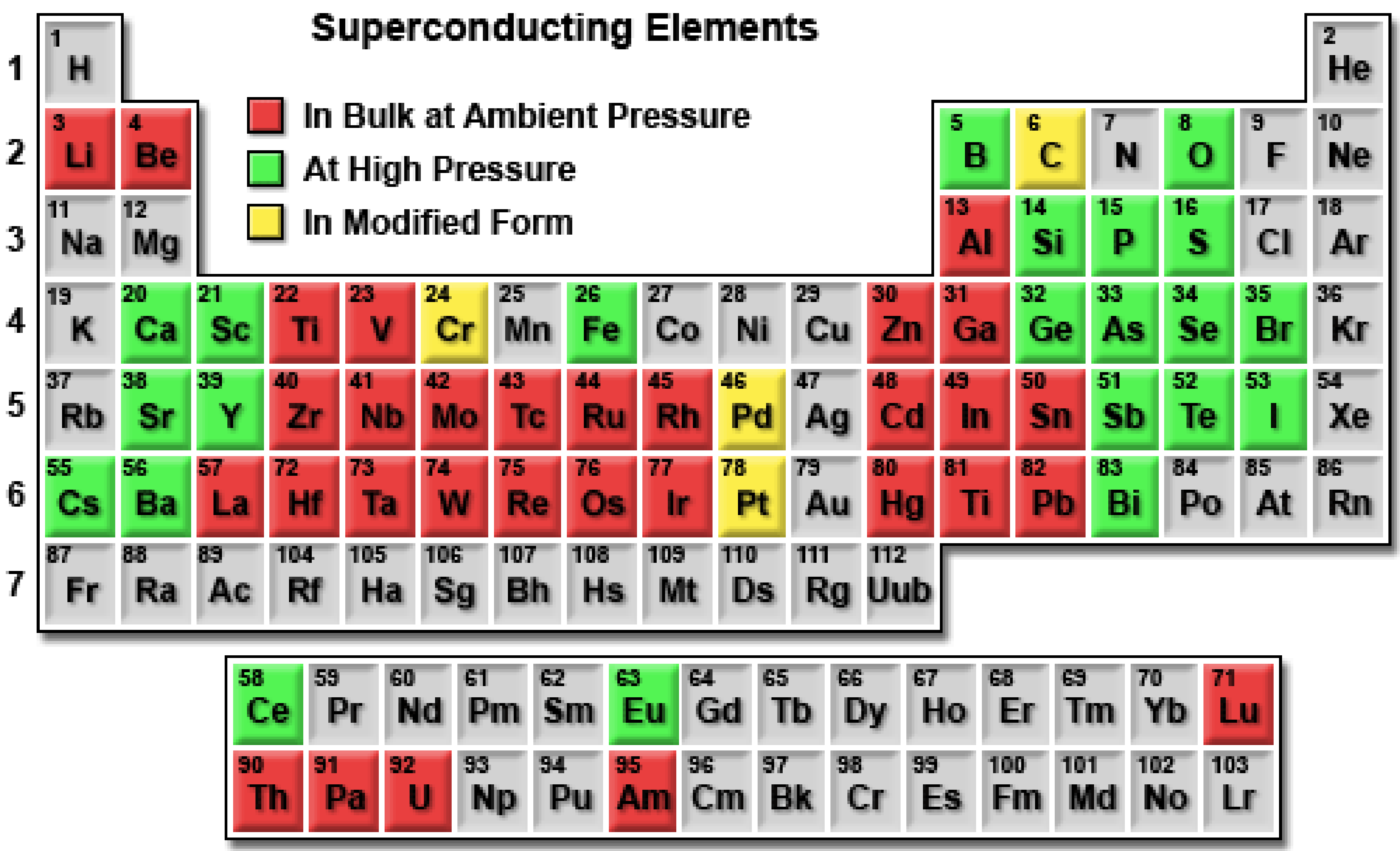
NbTi or Nb_3Sn

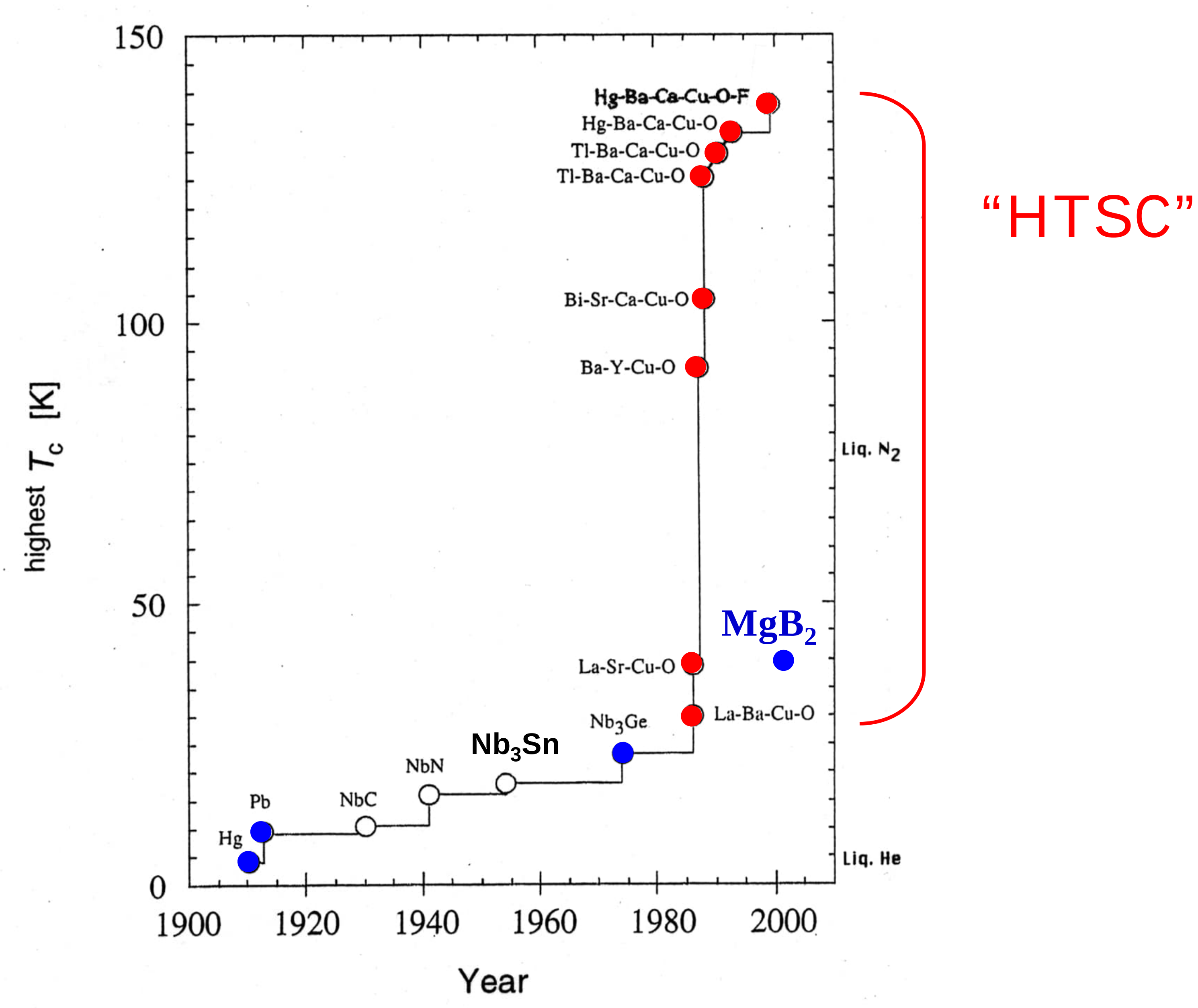


Superconducting Magnets

Super-Maglev Train

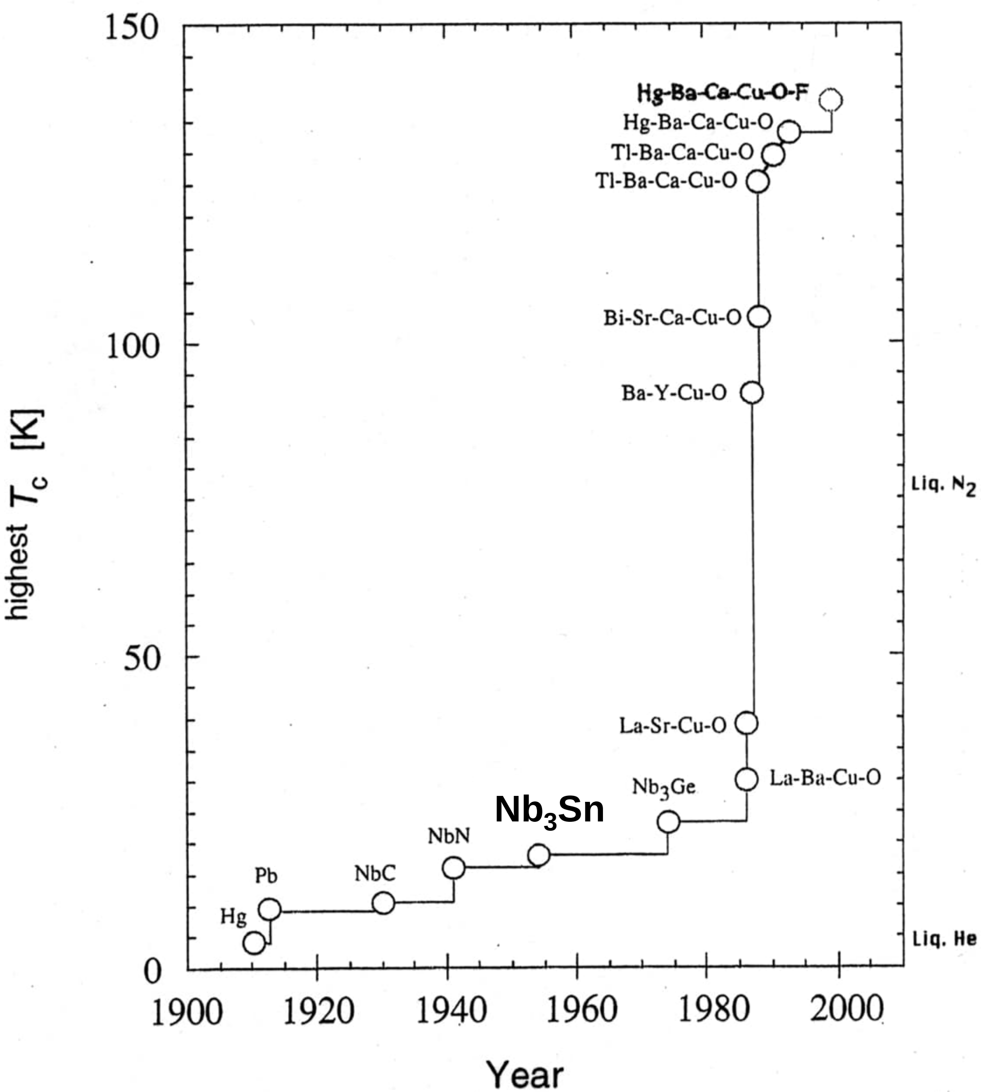
- 603 km / hour
- Test line 42.8 km


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-Ba-Ca-Cu-O-F
Hg-Ba-Ca-Cu-O
Tl-Ba-Ca-Cu-O
Tl-Ba-Ca-Cu-O
Bi-Sr-Ca-Cu-O
Ba-Y-Cu-O
Liq. N_2
MgB_2
La-Sr-Cu-O
La-Ba-Cu-O
Nb_3Ge
Nb_3Sn
NbN
NbC
Pb
Hg
Liq. He
"HTSC"

Search for new high-T_c superconductors



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

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

$YBa_2Cu_3O_7$

$Bi_2Sr_2Ca_2Cu_3O_{10}$

$Tl_2Ba_2Ca_2Cu_3O_{10}$

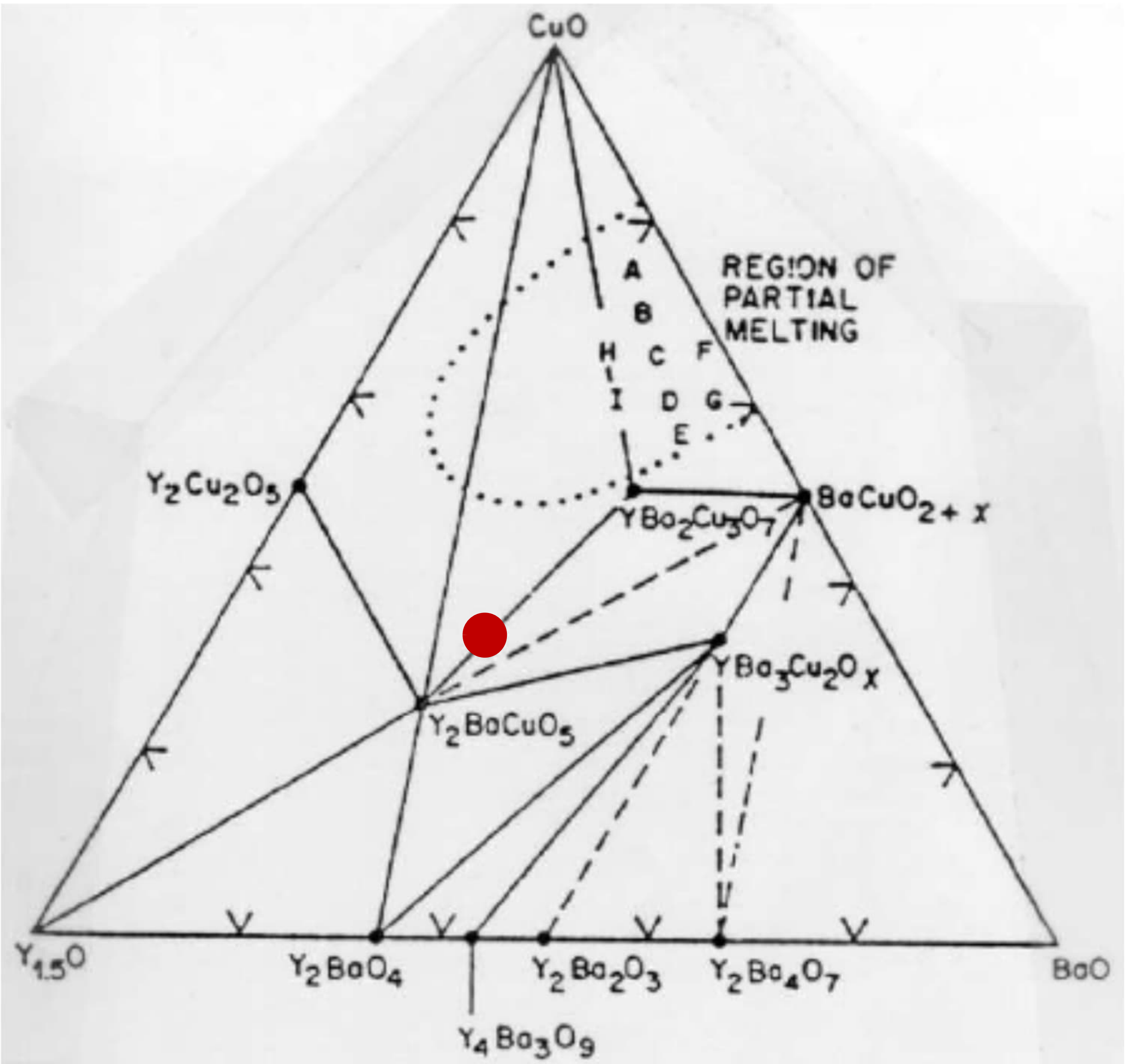
$TlBa_2Ca_2Cu_3O_9$

$HgBa_2Ca_2Cu_3O_9$

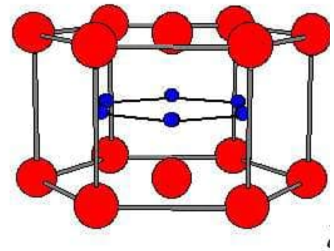
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIA or 0
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 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
Period 6	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
Period 7	87 Fr	88 Ra	89 to 103	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt									

Lanthanide series →	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
Actinide series →	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

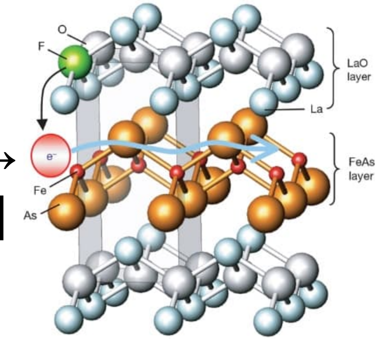
Pseudoternary Y-Ba-Cu-O Phasediagram ($0.5Y_2O_3$-BaO-CuO): 1000 °C, 1 atm O_2

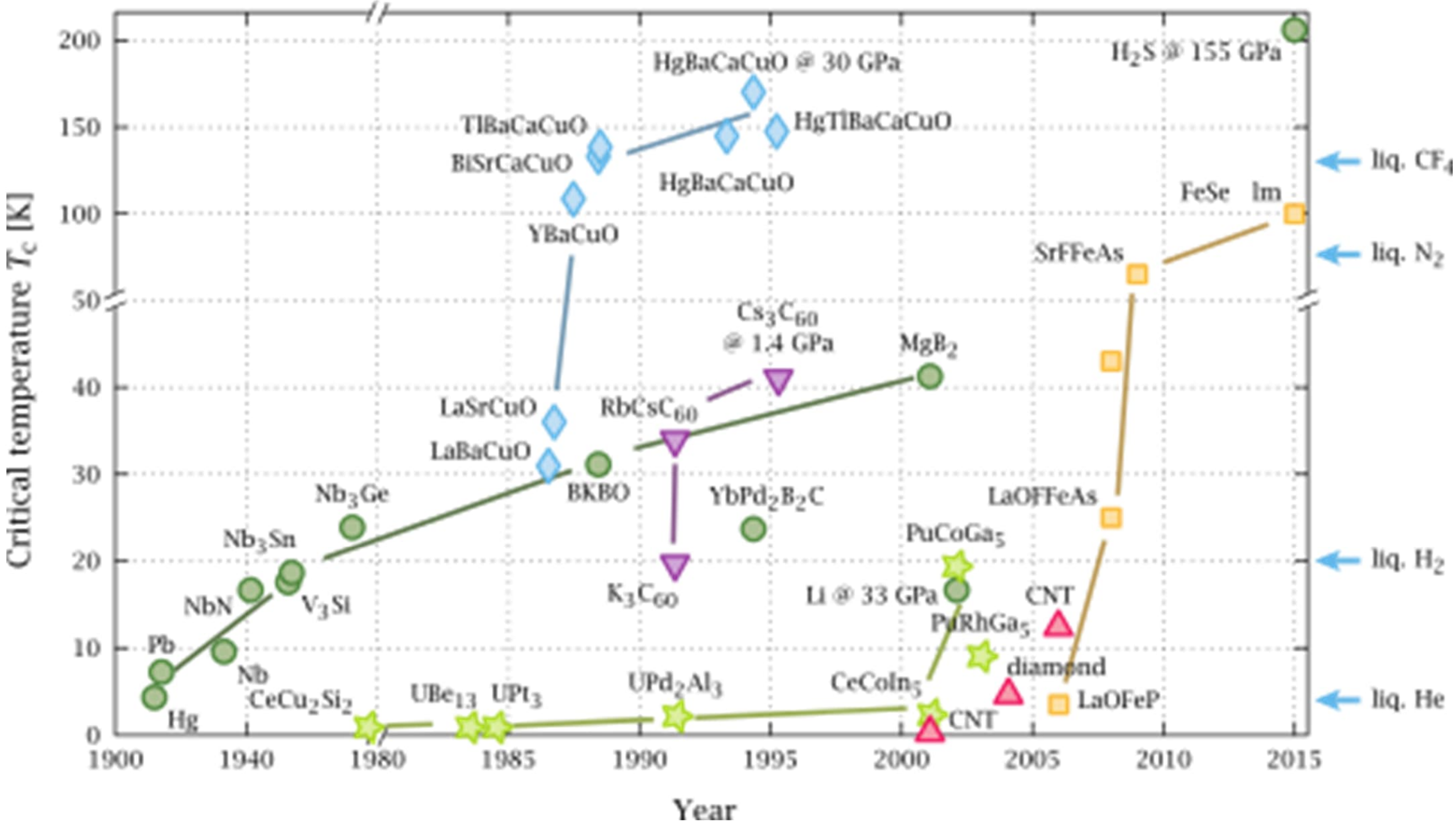


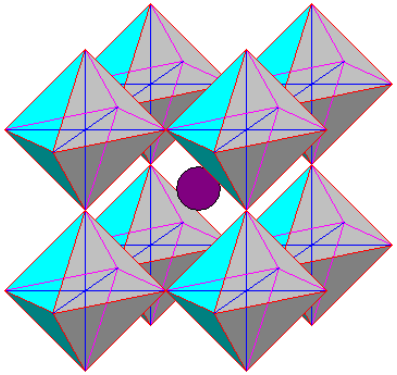
Akimitsu 2001:
MgB_2



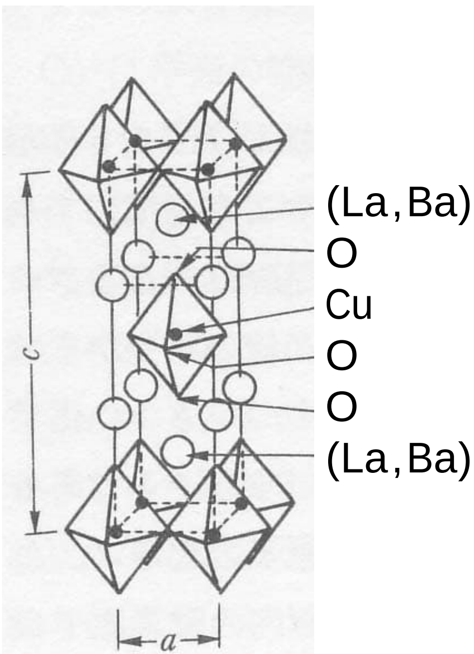
Hosono 2006 →
[La(O,F)][FeAs]

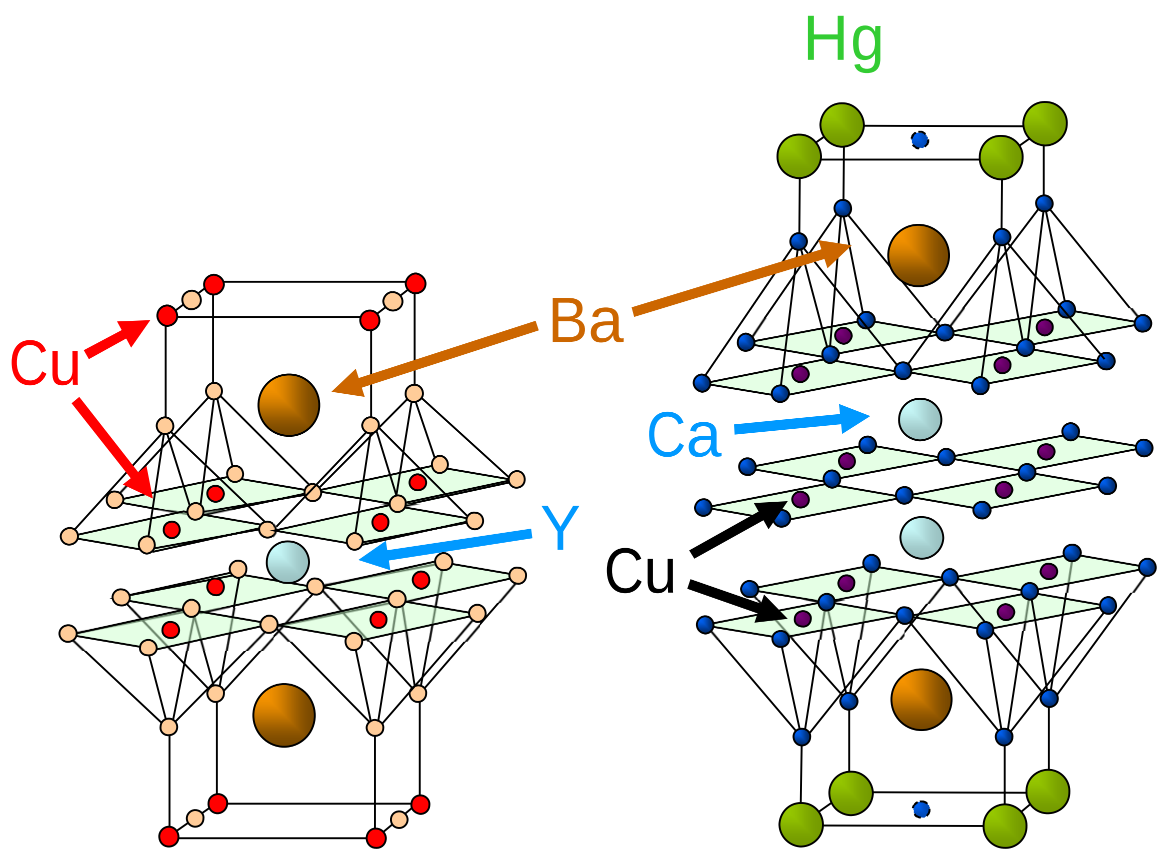






Crystal Structures of High-T_c Superconductive Copper Oxides

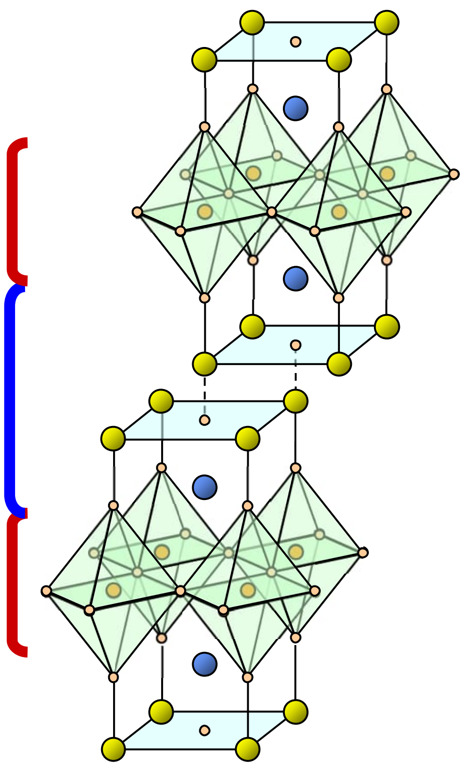


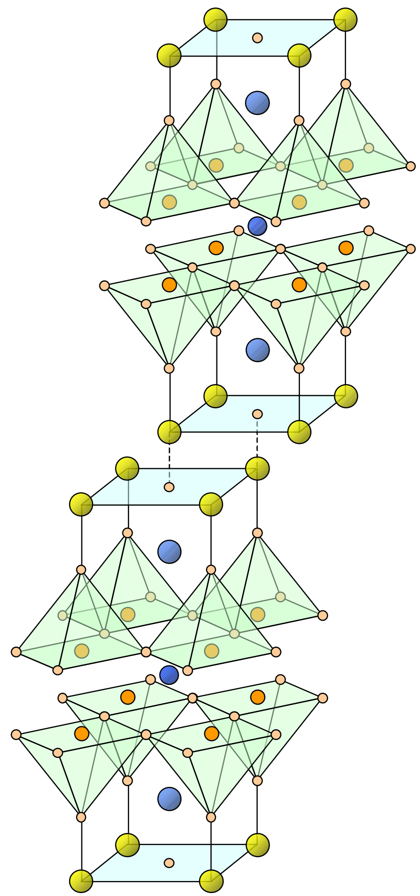


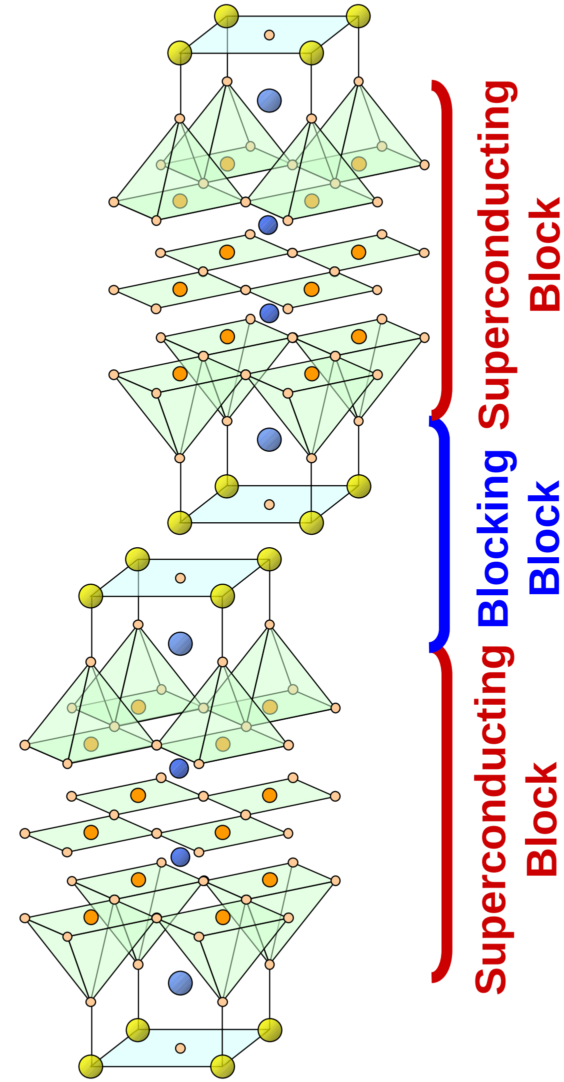
$(La,Ba)_2CuO_{4+\delta}$	$YBa_2Cu_3O_{7-\delta}$	$HgBa_2Ca_2Cu_3O_{9-\delta}$
$T_c \approx 35$ K	$T_c \approx 92$ K	$T_c \approx 135$ K

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-2201; $T_c \approx 20$ K

$Bi_2Sr_2CaCu_2O_{8+\delta}$

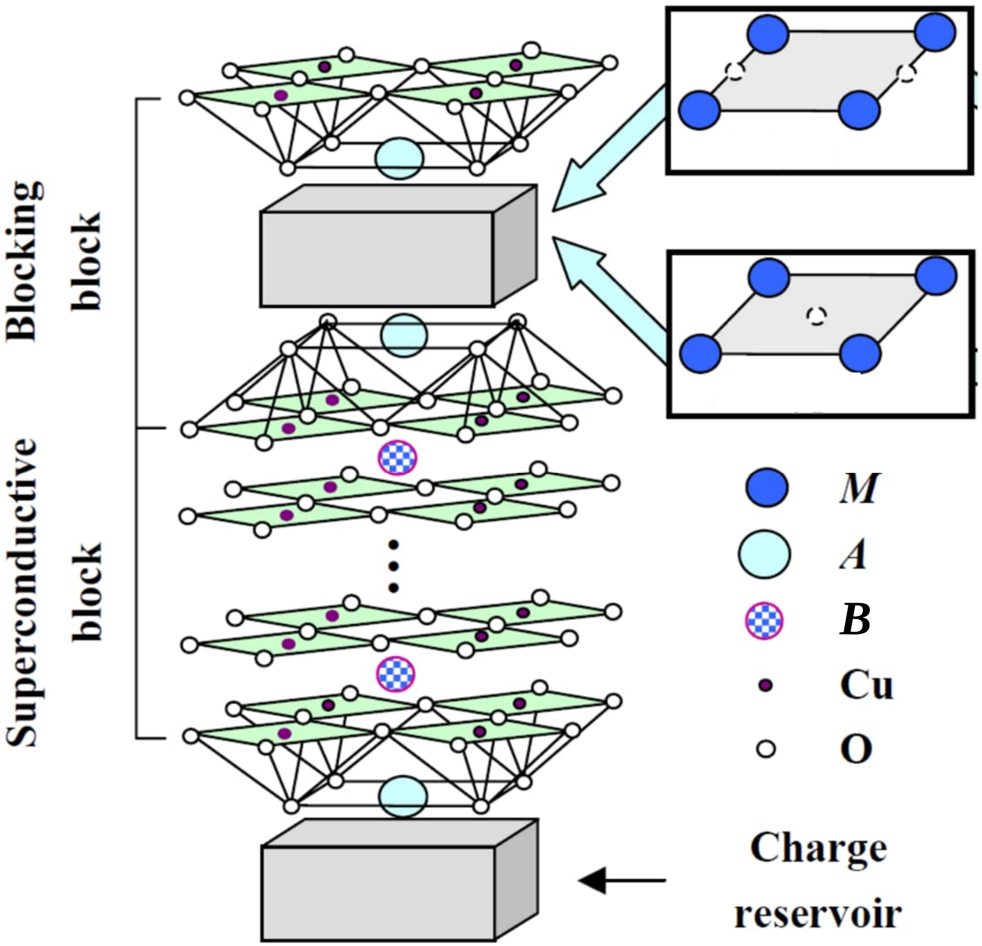
Bi-2212; $T_c \approx 80$ K

$Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$

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

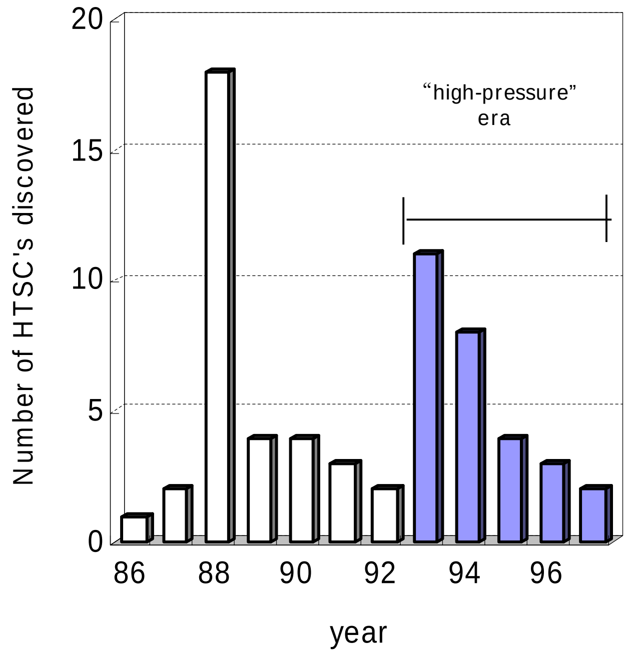


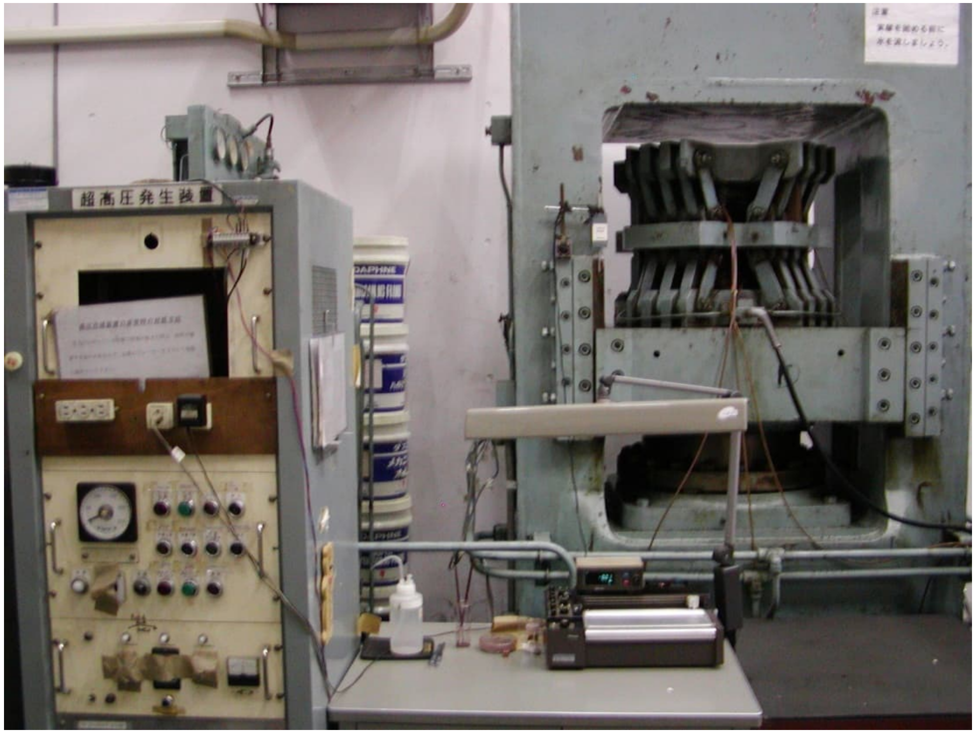
m x $MO_{1\pm\delta}$ layers

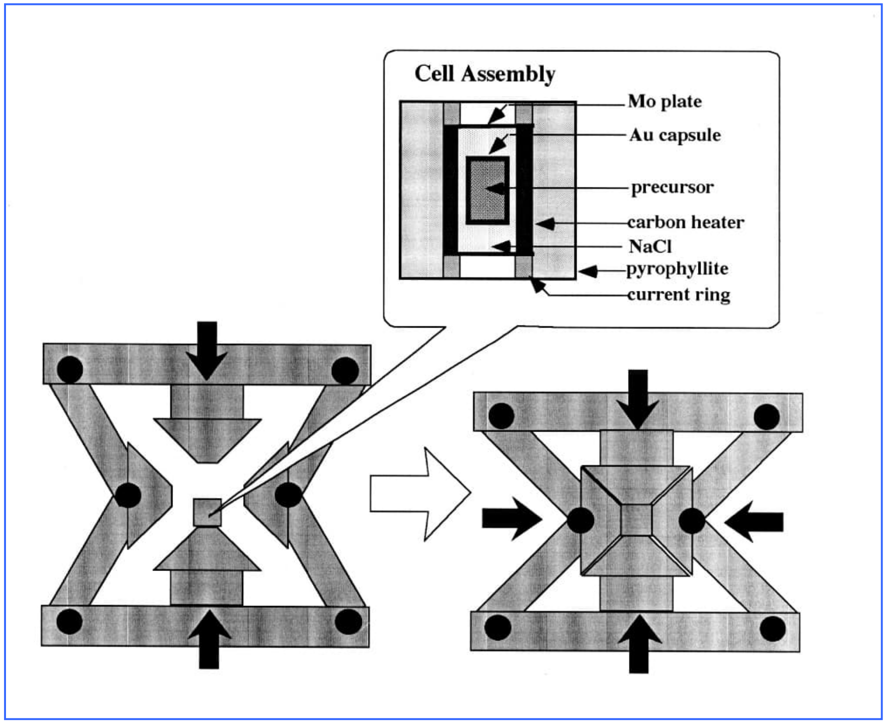
M. Karppinen & H. Yamauchi,
Control of the charge inhomogeneity and high-T_c superconducting properties in homologous series of multi-layered copper oxides,
Mater. Sci. Eng. R **26**, 51-96 (1999).

Ultra-High-Pressure Synthesis

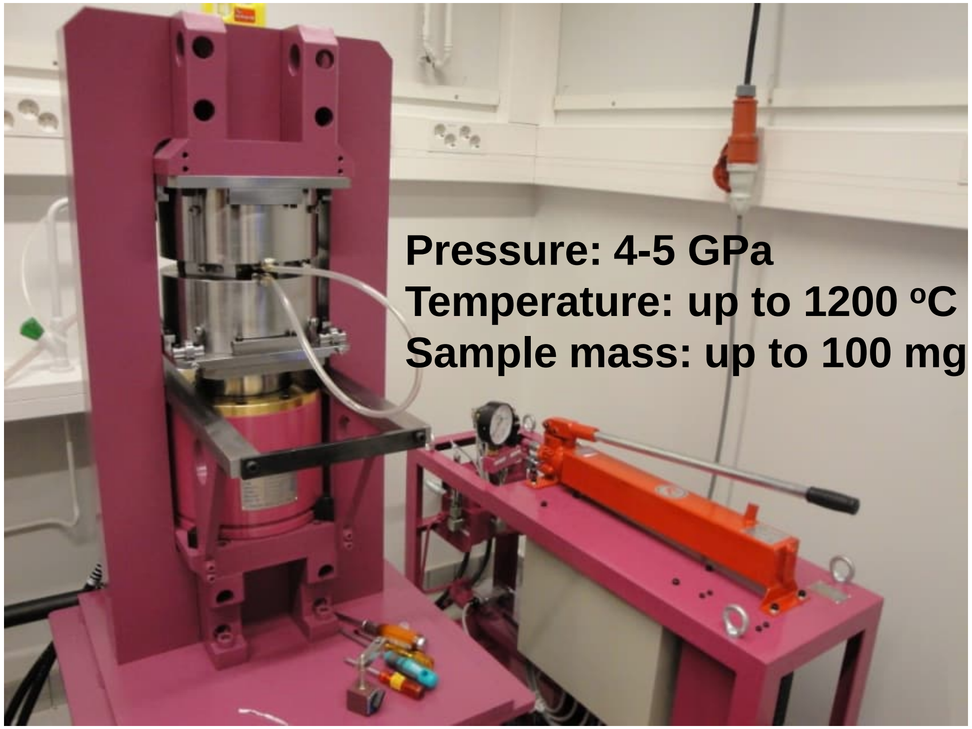
pressure: 2 ~ 8 GPa
sample: 50 ~ 300 mg



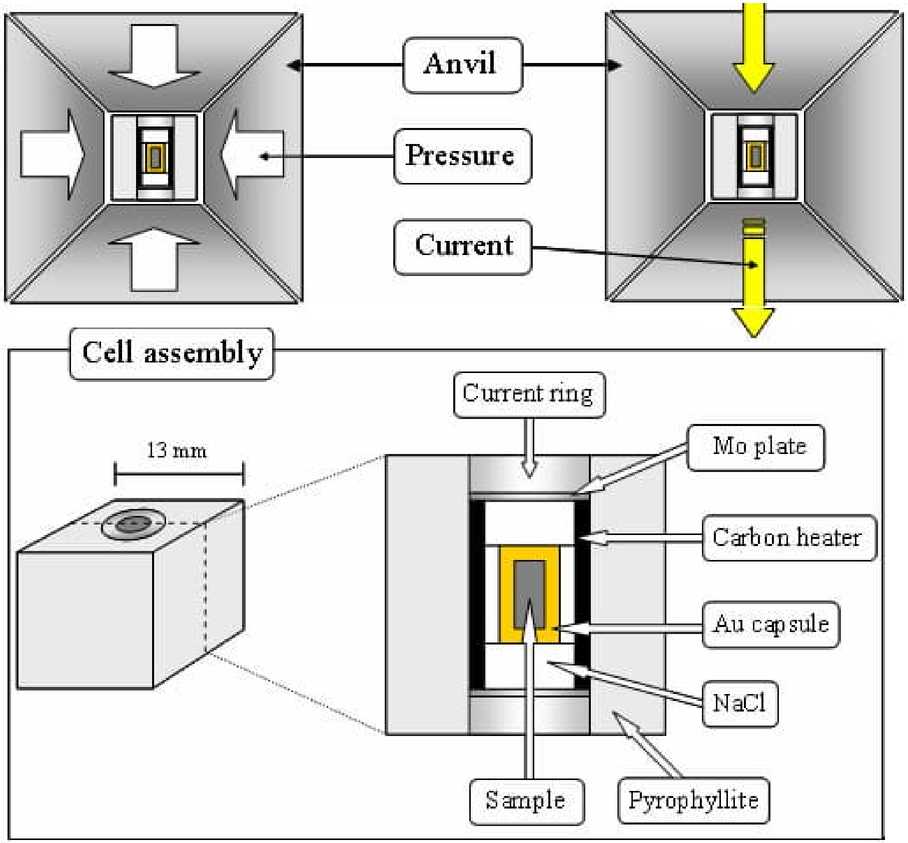


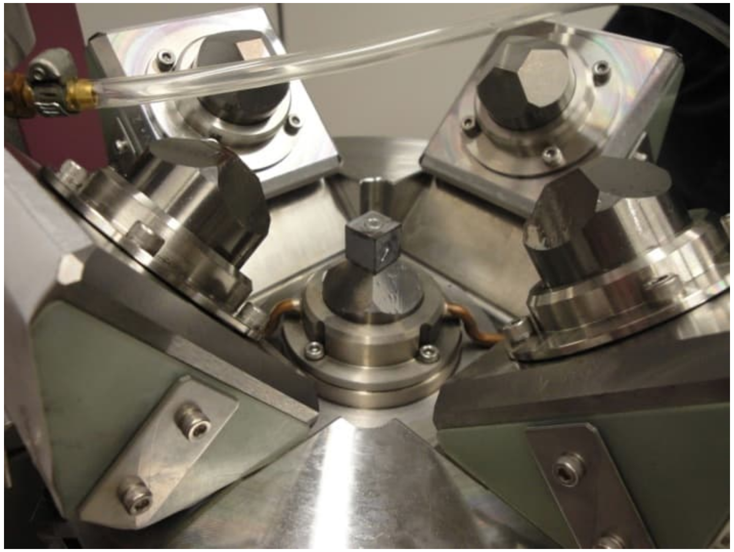


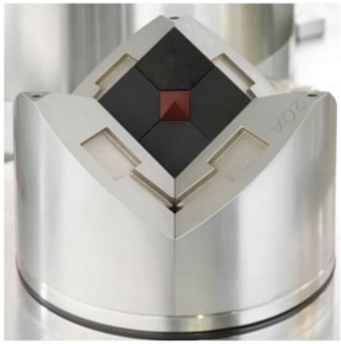
OUR HIGH-PRESSURE EQUIPMENT



Pressure: 4-5 GPa
Temperature: up to 1200 ºC
Sample mass: up to 100 mg







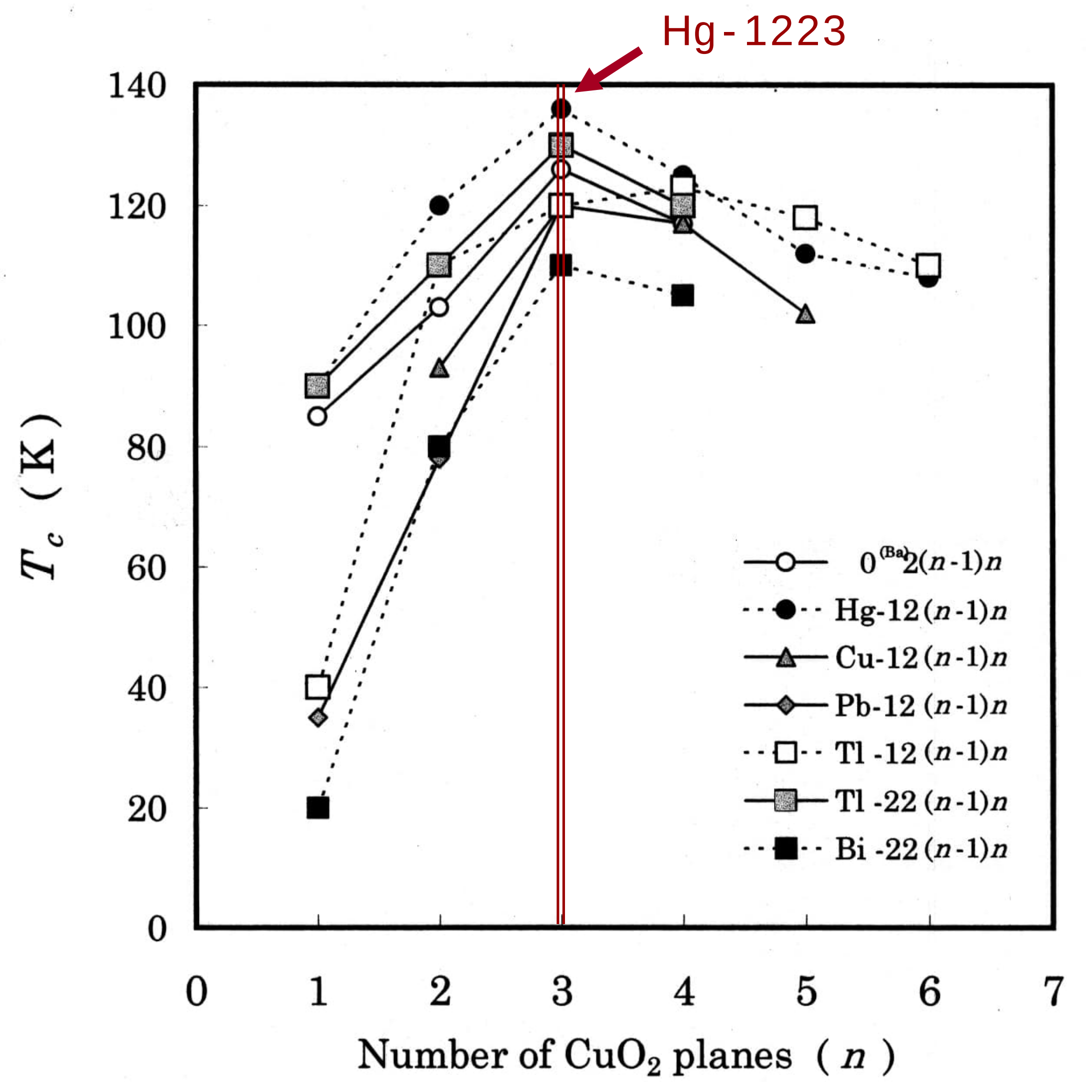
$M_mA_2Q_{n-1}Cu_nO_{m+2+2n+\delta}$

M-m2(n-1)n

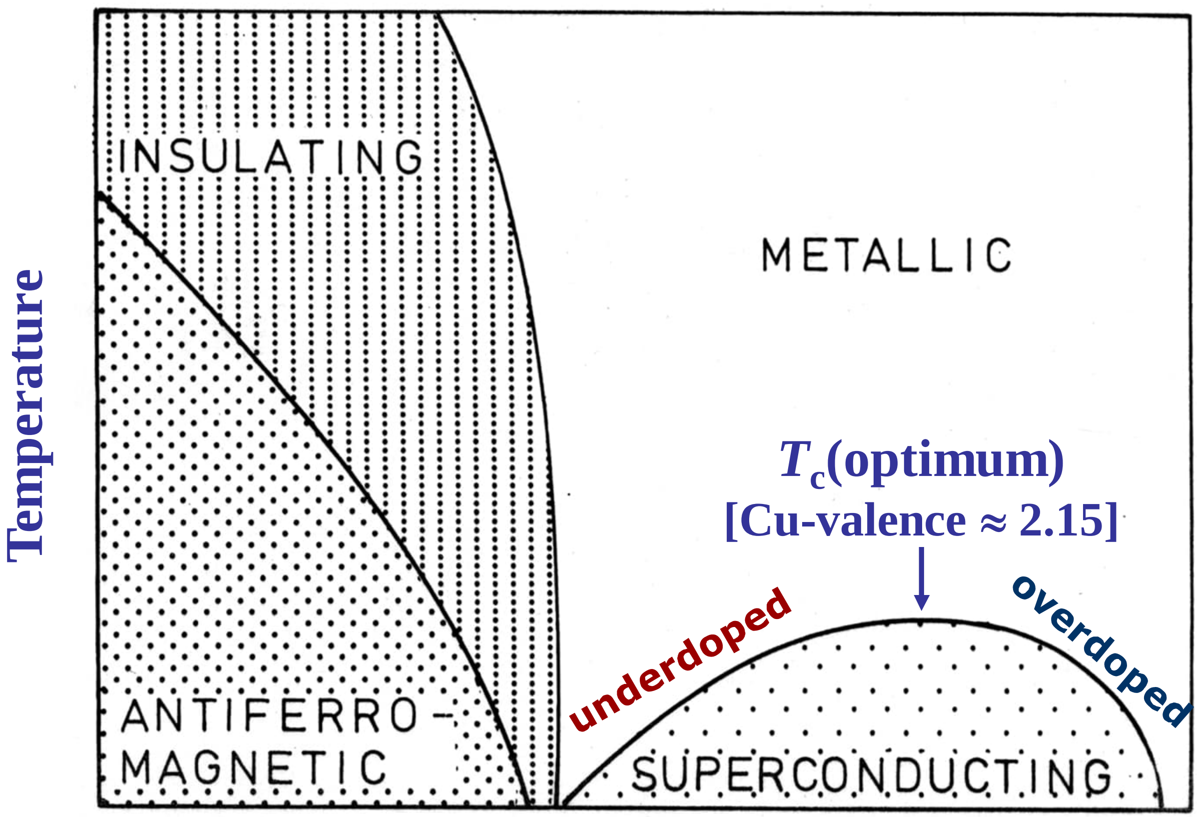
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48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



CuO_2-plane hole concentration [p(CuO_2)]

Valence of copper [V(Cu)]

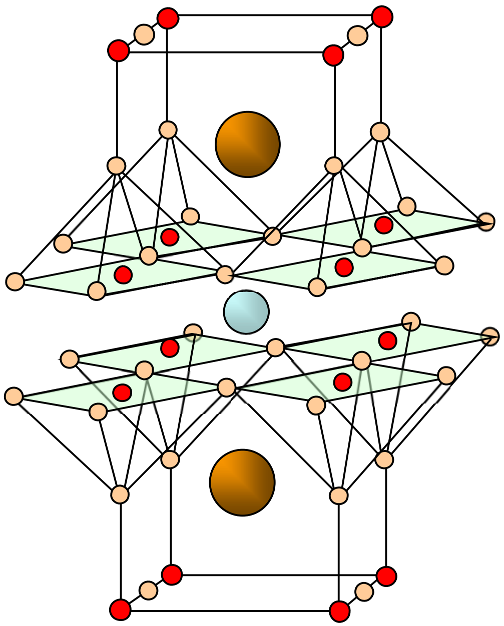
⇧

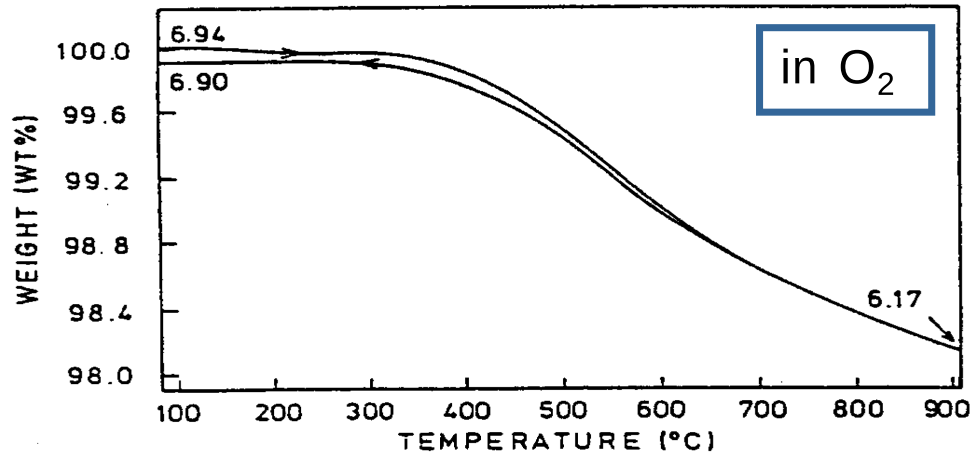
Chemistry

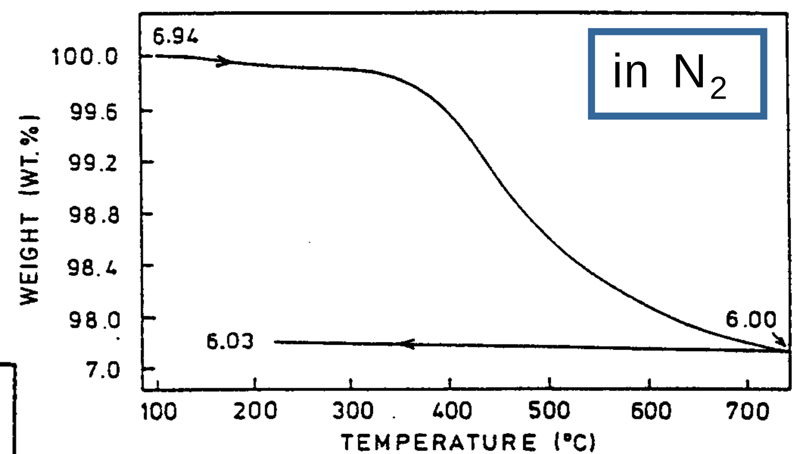
Hole-carrier concentration

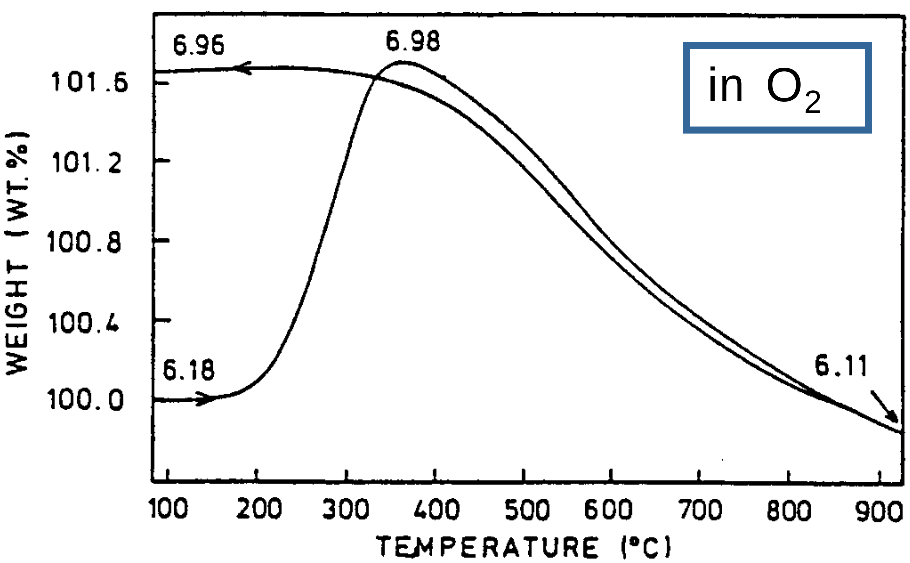
p(CuO_2) = V(Cu)-2

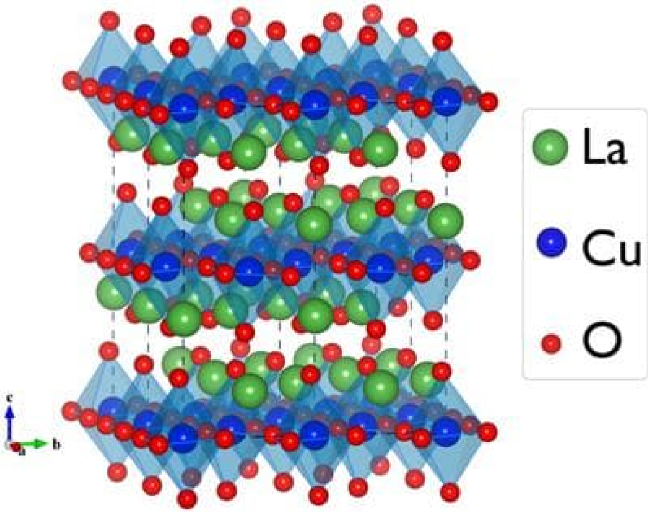
$CuBa_2YCu_2O_{7-\delta}$





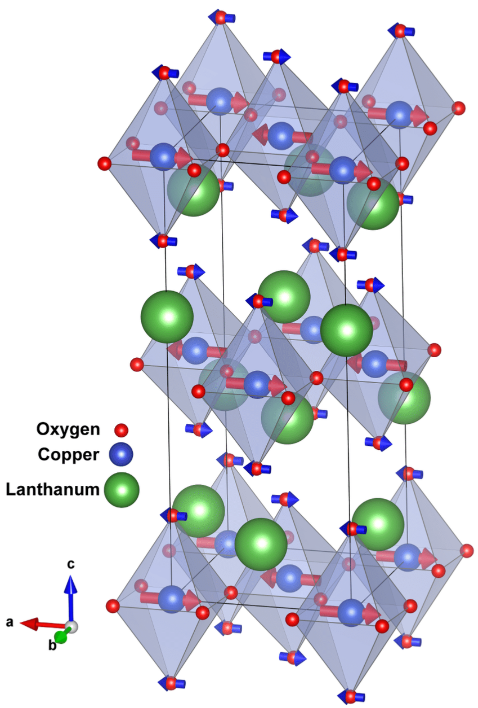


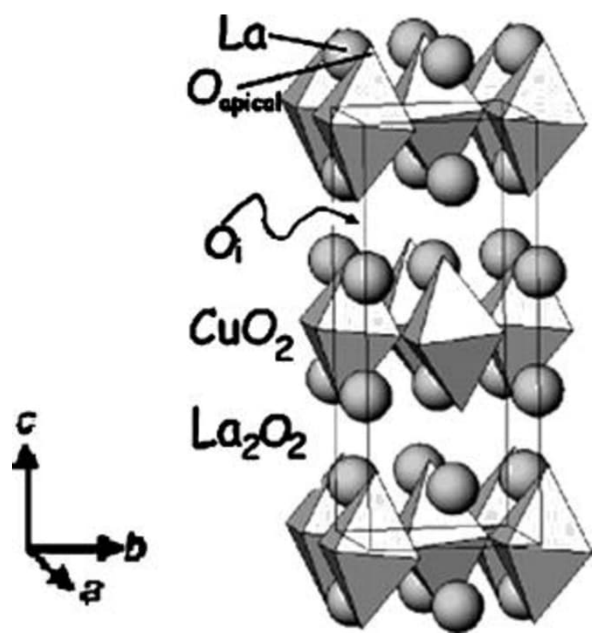


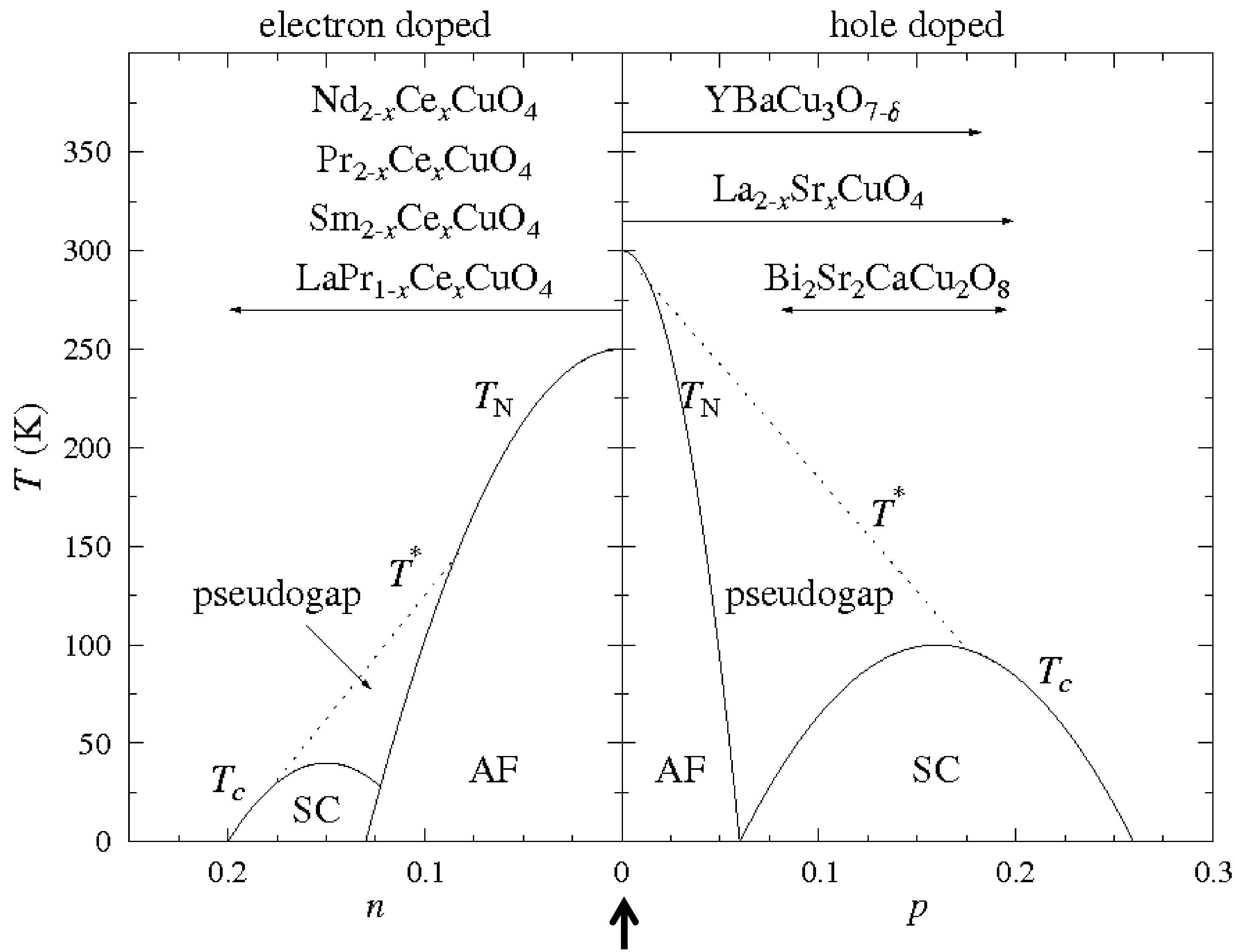


La_2CuO_4

- 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

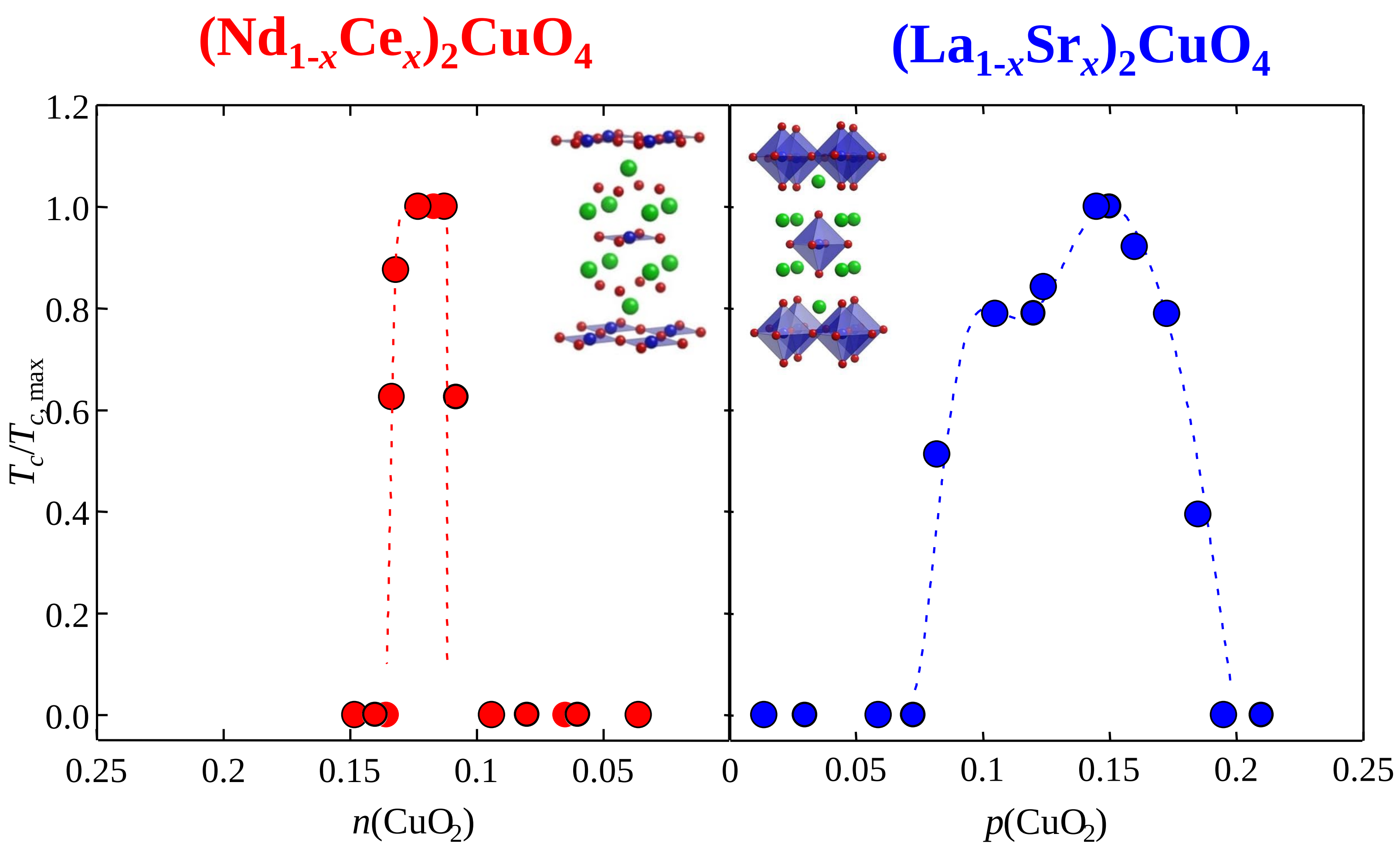






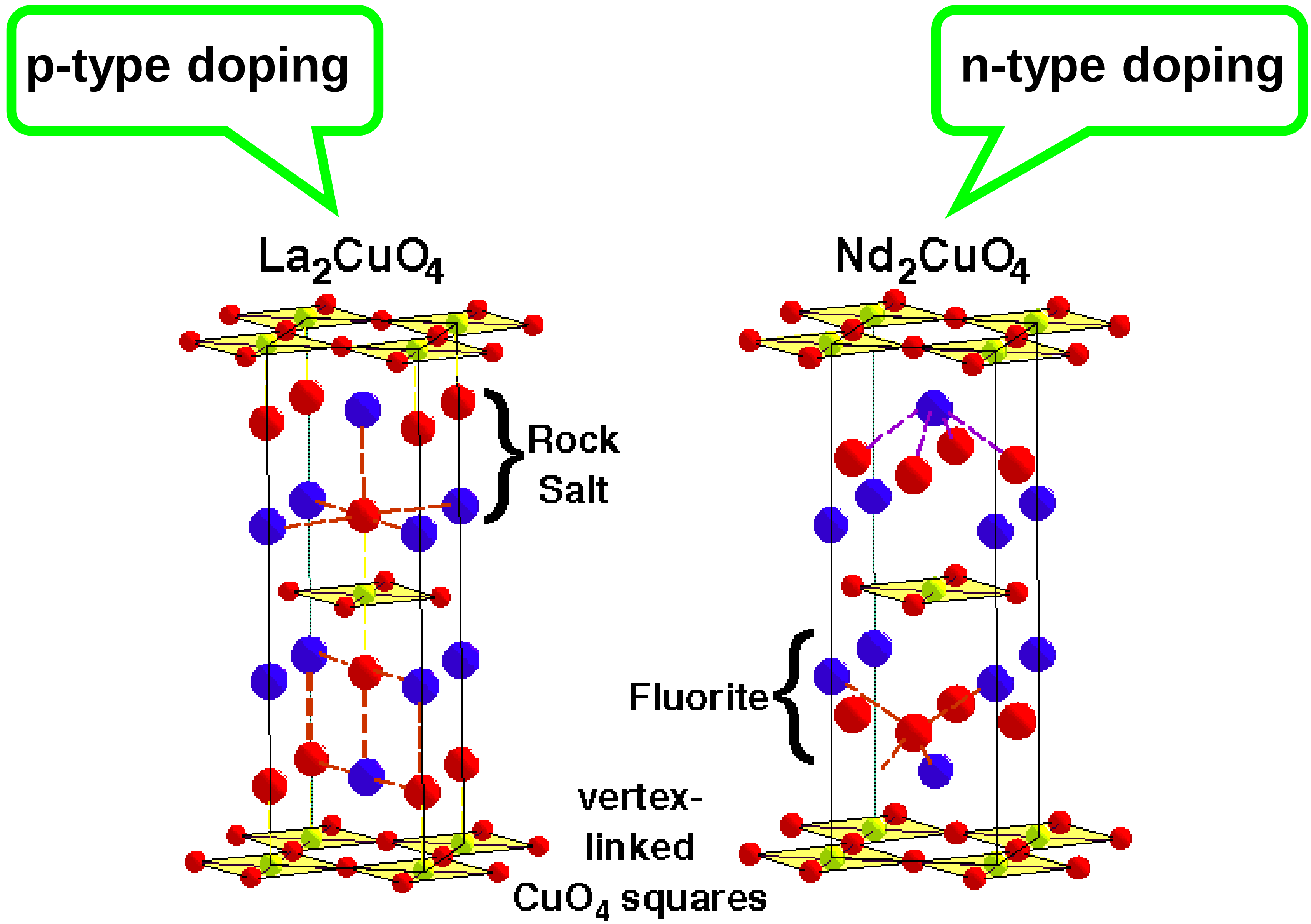
n = electron density = 2 - V(Cu) V(Cu) = 2 *p* = hole density = V(Cu) - 2

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



$n(\mathrm{CuO_2}) \equiv 2 - V(\mathrm{Cu})$

$p(\mathrm{CuO_2}) \equiv V(\mathrm{Cu}) - 2$


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