

Functional Inorganic Materials

Fall 2023

Mondays: 10.15 - 12.00
Thursdays: 10.15 - 12.00

Lecture hall locations: U7 in Otakaari 1 / U-wing
Ke1 in Kemistintie 1 (CHEM building)

You can use <https://usefulaaltomap.fi/> to see the exact location of U7.

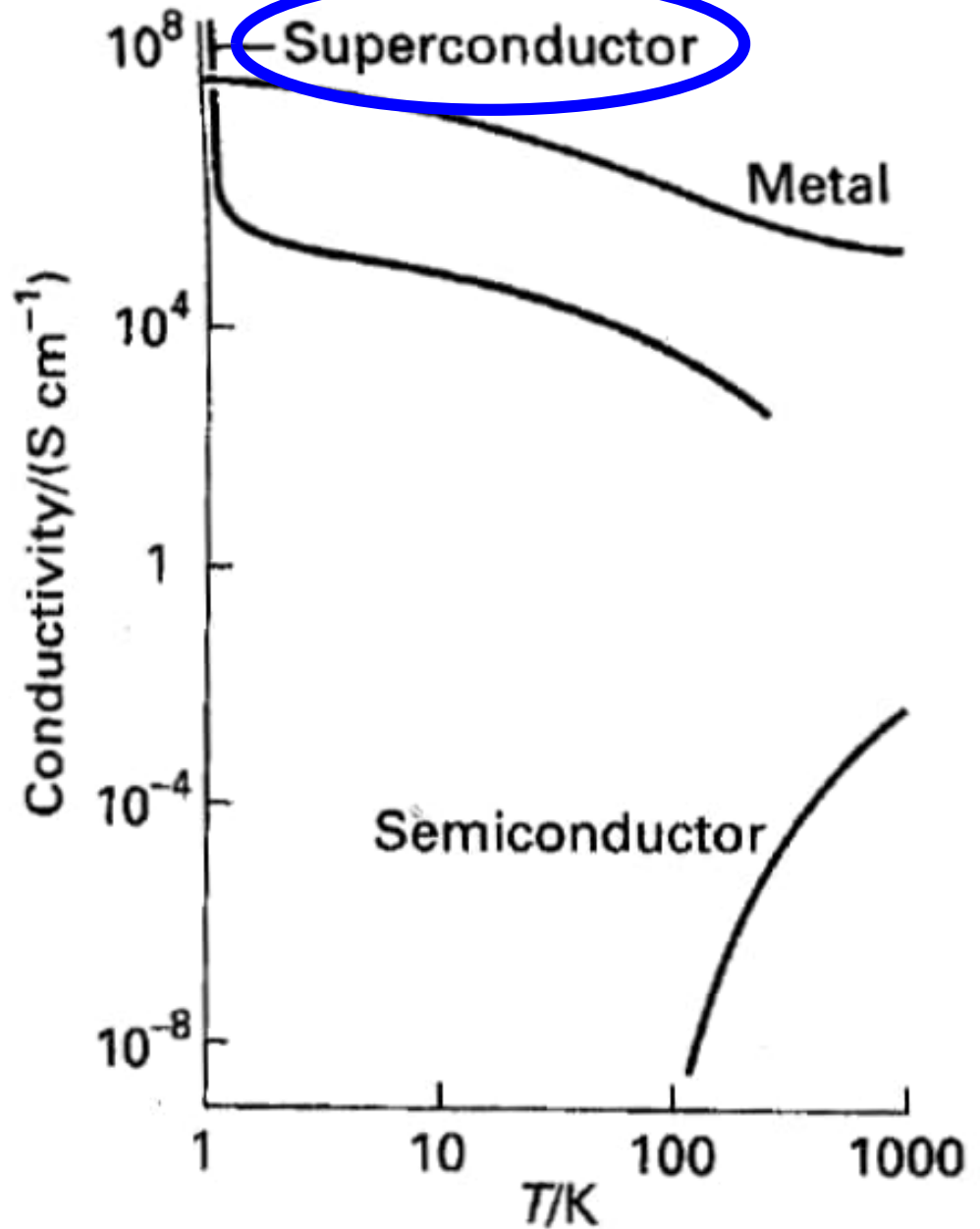
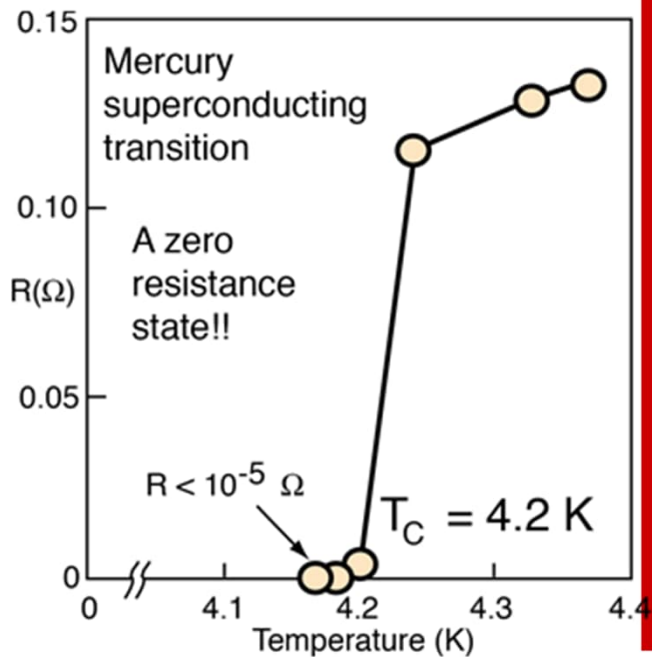
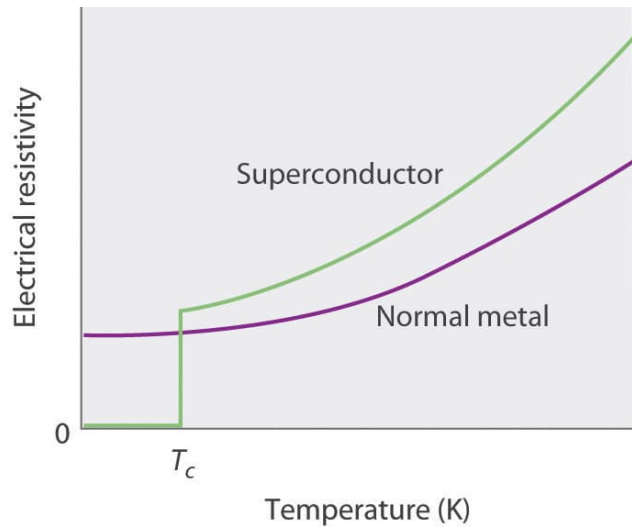
#	Date	Place	Who	Topic
1	Mon 4.9.	U7 (U135a)	Maarit	Introduction + Materials design
2	Thu 7.9.	Ke1 (A305)	Antti	Introduction + Computational materials design
3	Mon 11.9.	U7 (U135a)	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	Thu 14.9.	Ke1 (A305)	Maarit	Magnetic oxides
5	Mon 18.9.	U7 (U135a)	Maarit	Ionic conductivity (Oxygen): Oxygen storage and SOFC
6	Thu 21.9.	Ke1 (A305)	Maarit	Ionic conductivity (Lithium): Li-ion battery
7	Mon 25.9.	U7 (U135a)	Antti	Thermal conductivity
8	Thu 28.9.	Ke1 (A305)	Antti	Thermoelectricity
9	Mon 2.10.	U7 (U135a)	Antti	Piezoelectricity
10	Thu 5.10.	Ke1 (A305)	Antti	Pyroelectricity and ferroelectricity
11	Mon 9.10.	U7 (U135a)	Antti	Luminescent and optically active materials
12	Thu 12.10.	Ke1 (A305)	Maarit	Hybrid materials

LECTURE 3: (High- T_c) Superconductivity/conductors

- ❖ 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 / 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: $\text{YBa}_2\text{Cu}_3\text{O}_{7\pm\delta}$, $\text{Bi}_2\text{Sr}_2\text{CuO}_{6\pm\delta}$, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8\pm\delta}$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10\pm\delta}$
 - 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. **SELECT ONE OF THE FOLLOWING TWO TASKS (A or B):**
 - A. Nb_3Sn and Nb_3Ge are important low-temperature superconductors and members of the so-called A15 family of intermetallic compounds discovered already in 1950s. Please search for further information and write a short essay with few references of these materials.
 - B. This summer a report on possible room-temperature superconductor was submitted for publication by Korean researchers. This report immediately arouse wide excitement within the superconductor researcher community. Please, write few sentences about the discovery (which material, etc.) and try to look for further news (from internet) whether these initial exciting news have been confirmed (or denied) by other researchers.



SUPERCONDUCTIVITY

Superconductivity

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



Nobel 1913

Meissner effect

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



High- T_c superconductivity

- 1986: Bednorz and Müller
- $(\text{La,Ba})_2\text{CuO}_4$ ($T_c = 30\sim 40$ K)



Nobel 1987

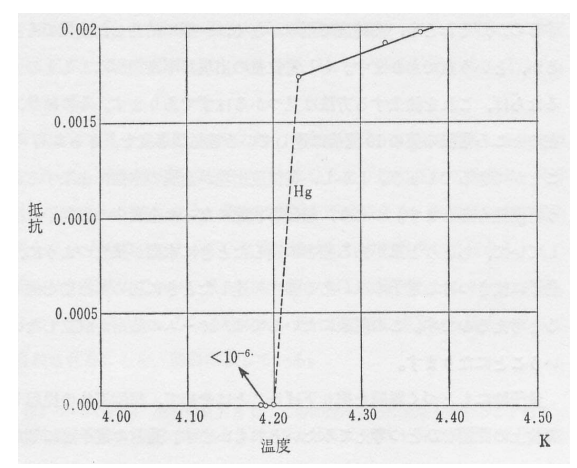
Present record in T_c :

138 K for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$

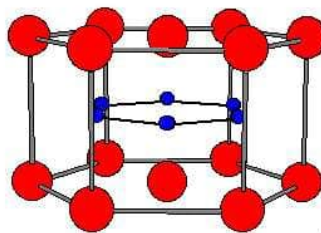


Kamerlingh-Onnes Institute,
@University of Leiden, the Netherlands

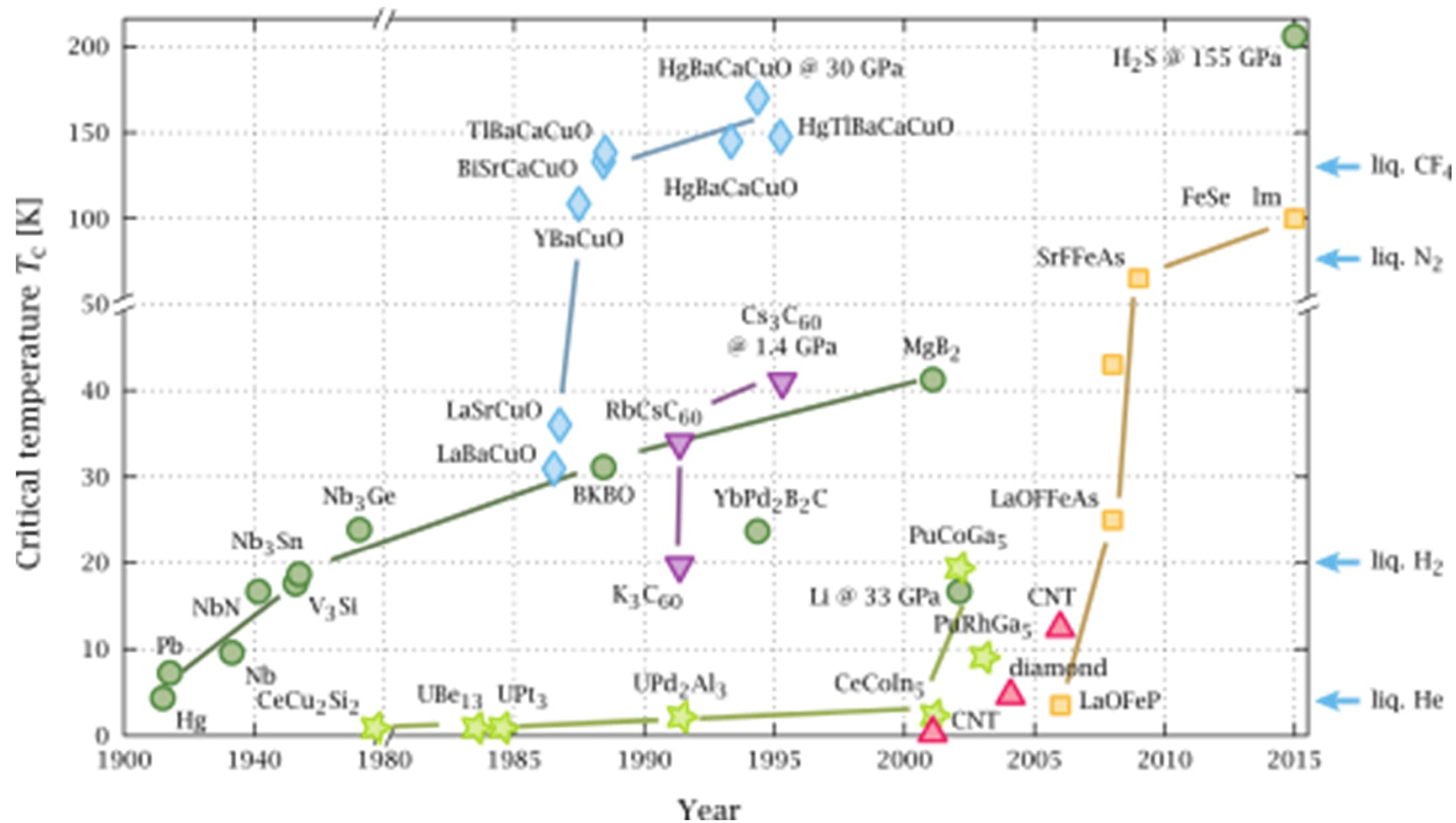
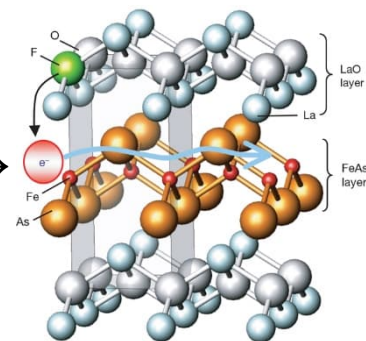
Heike Kamerlingh-Onnes and J.D. van der Waals



Akimitsu 2001:
MgB₂



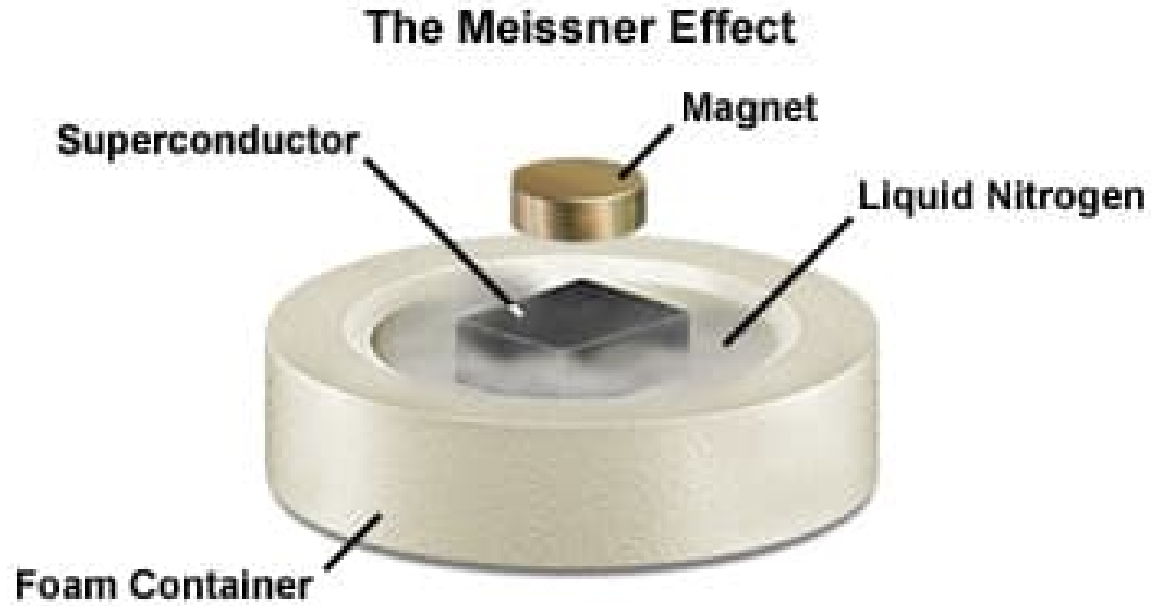
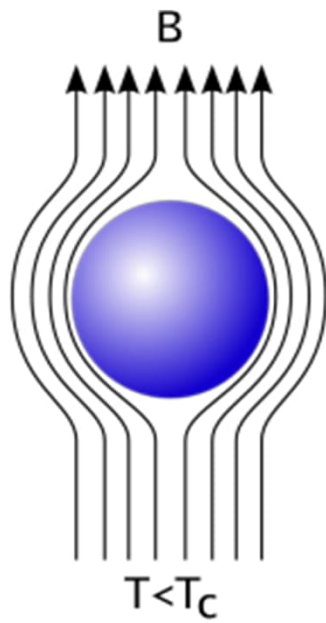
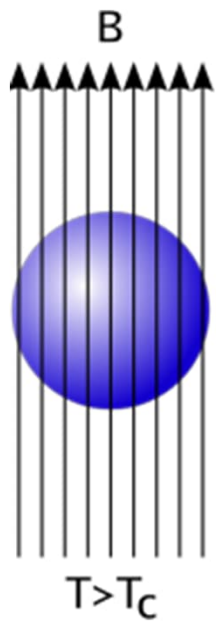
Hosono 2006 →
[La(O,F)][FeAs]



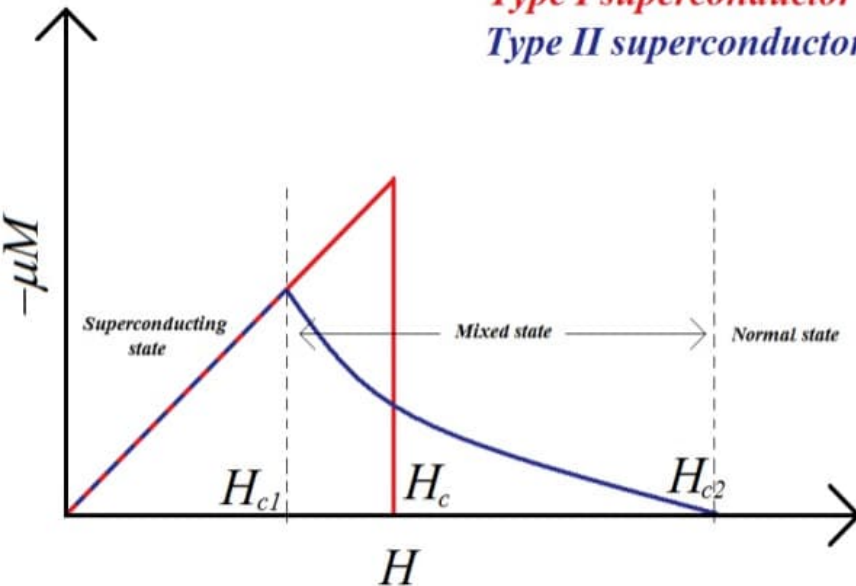
**The first room-temperature ambient-pressure
superconductor,**

Sukbae Lee, Ji-Hoon Kim & Young-Wan Kwon,

<https://arxiv.org/abs/2307.12008>



Type I superconductor
Type II superconductor



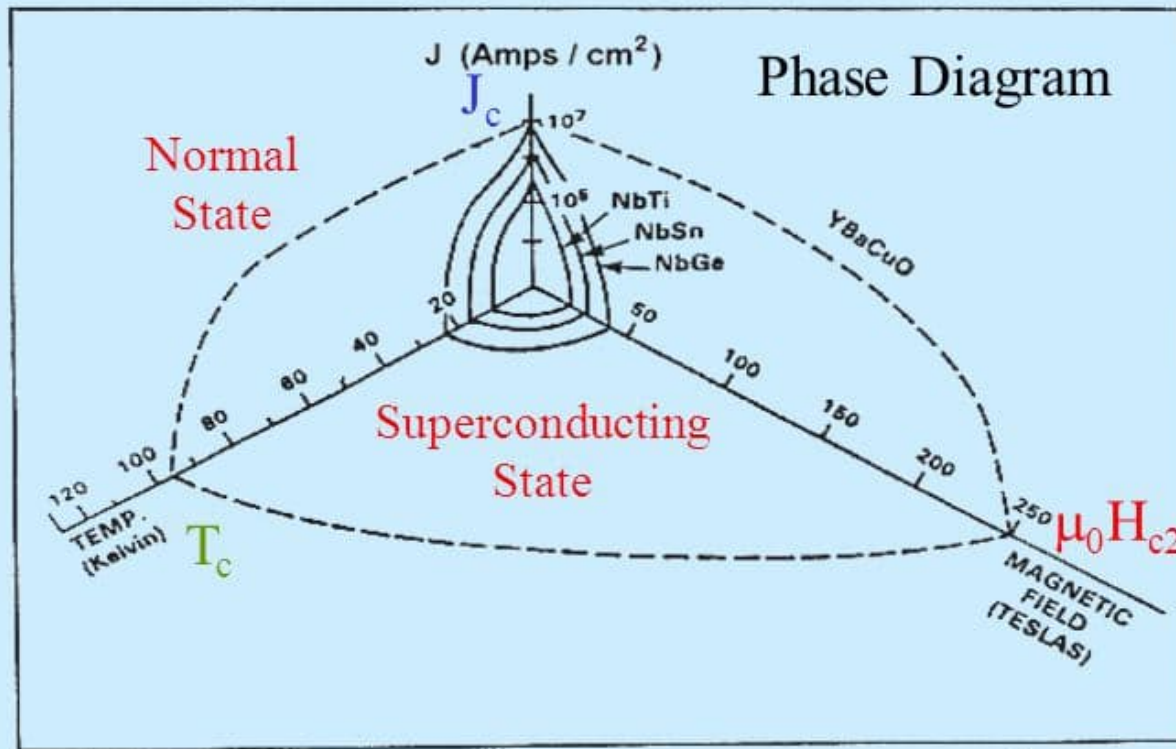
Type-1 Examples:

- Hg, Pb & most of the pure metals

Type-2 Examples:

- Nb, NbTi, Nb₃Sn & HTSCs

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

Superconductivity of Nb₃Sn

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 Nb₃Sn 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, V₃Si, 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 ratio³ 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 Nb₃Sn and Ta₃Sn both crystallize in a β -W structure with a lattice constant of about 5.3Å. The Ta₃Sn was measured in the apparatus previously described,⁴ and became superconducting near 6°K. The transition temperature of the Nb₃Sn 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 \pm 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

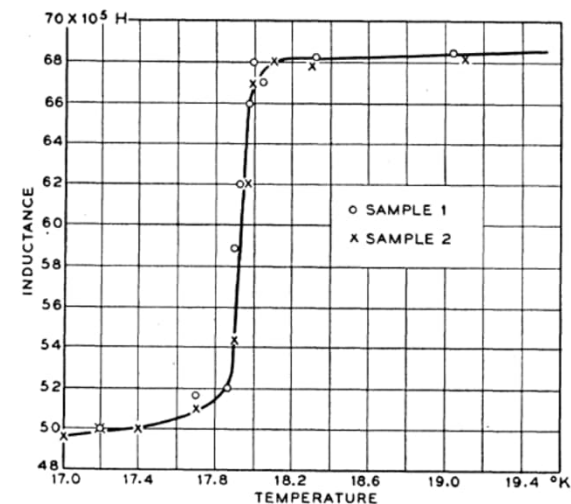


FIG. 1. Variation of susceptibility with temperature of Nb₃Sn.

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. Nb₃Sn and Ta₃Sn seem to be formed by a peritectic reaction between 1200°C and 1550°C.

¹ G. Hardy and J. K. Hulm, *Phys. Rev.* **89**, 884 (1953).

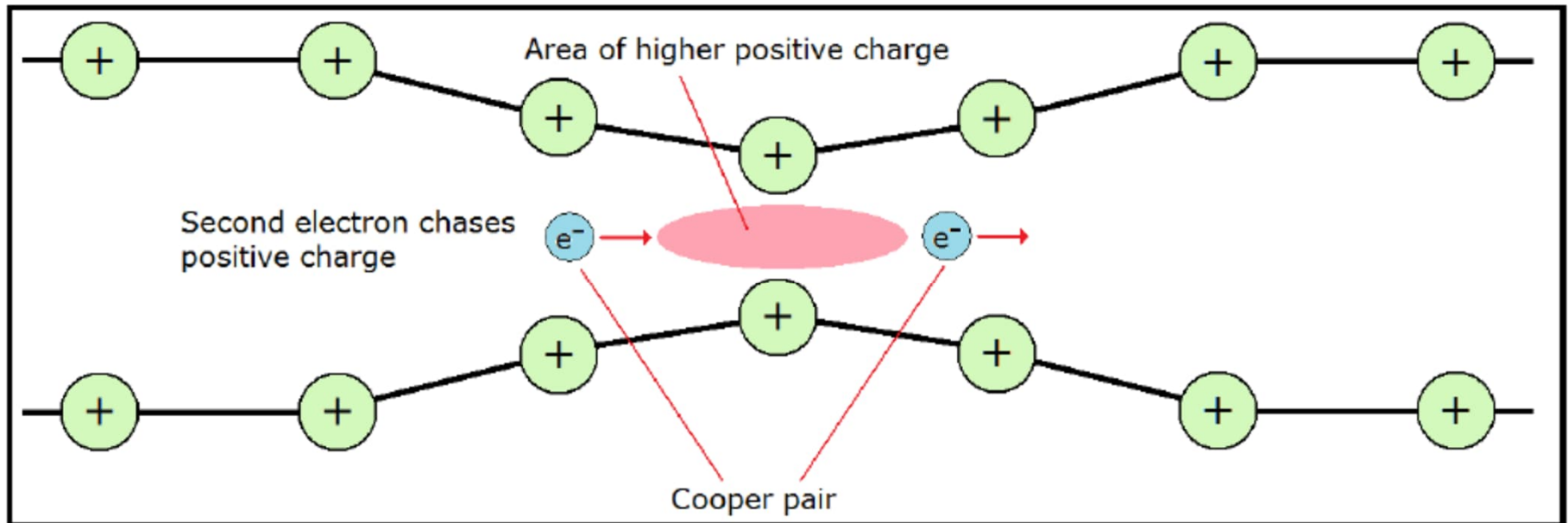
² H. I. Wallbaum, *Z. Metallkunde* **31**, 362 (1939).

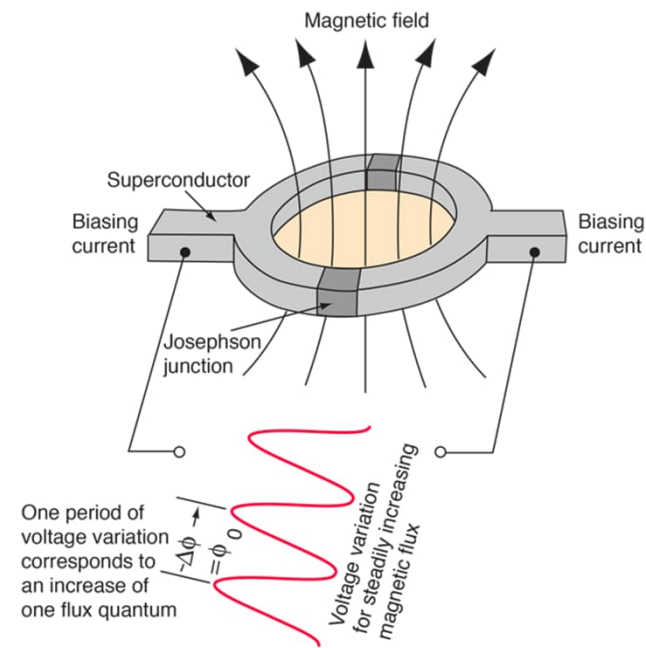
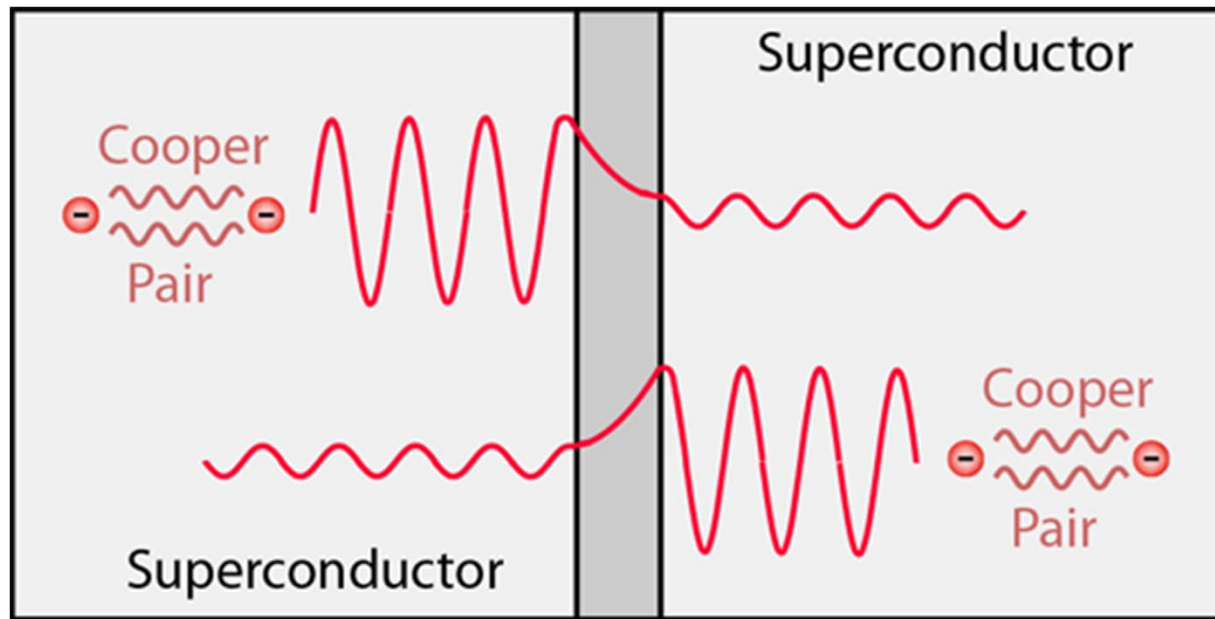
³ B. T. Matthias, *Phys. Rev.* **92**, 874 (1953).

⁴ B. T. Matthias and J. K. Hulm, *Phys. Rev.* **87**, 799 (1952).

Bardeen, Cooper & Schrieffer

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



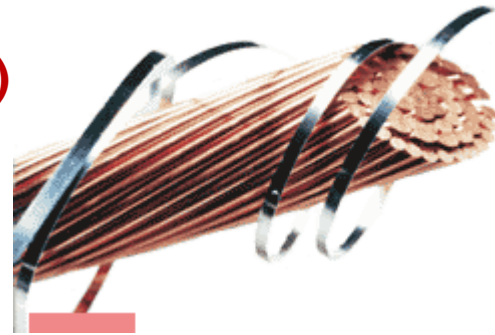


Josephson Junction & SQUID

- 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)

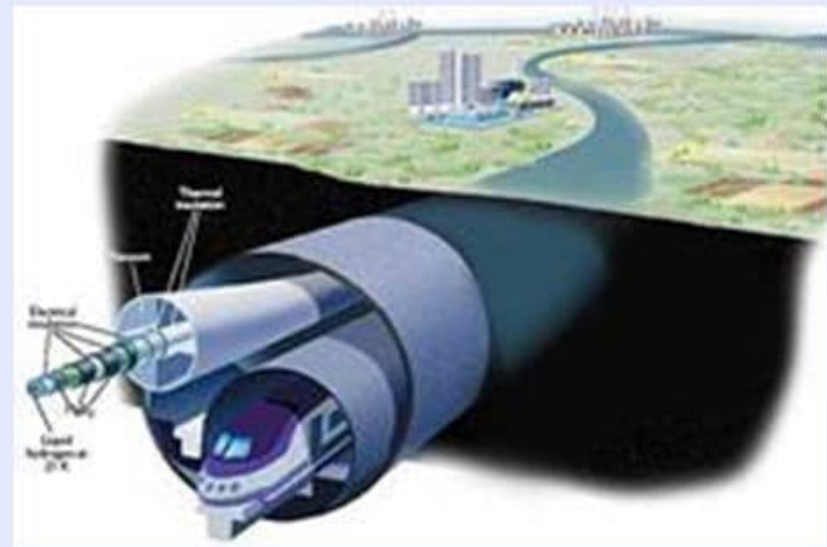
ZERO RESISTIVE LOSSES

22

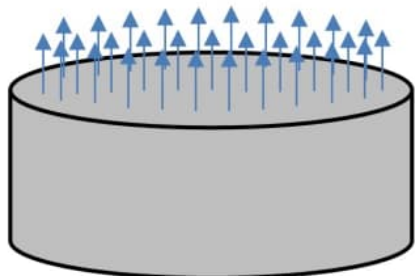
Applications using Superconductors

Superconducting power transmission

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



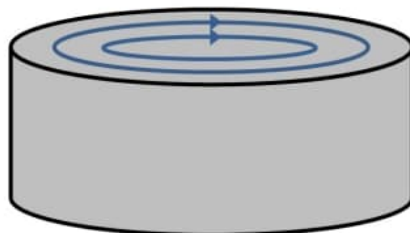
STRONG MAGNETS



Permanent ferromagnet

Spin

Neodymium N-B-Fe (1.5 T)

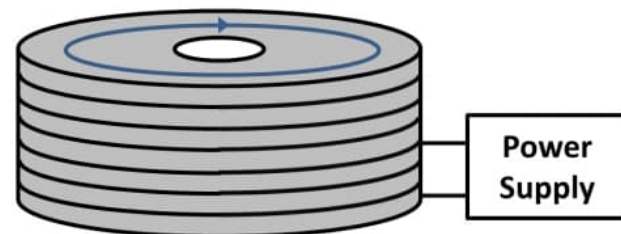


Bulk superconductor

Induced, superconducting

loop current

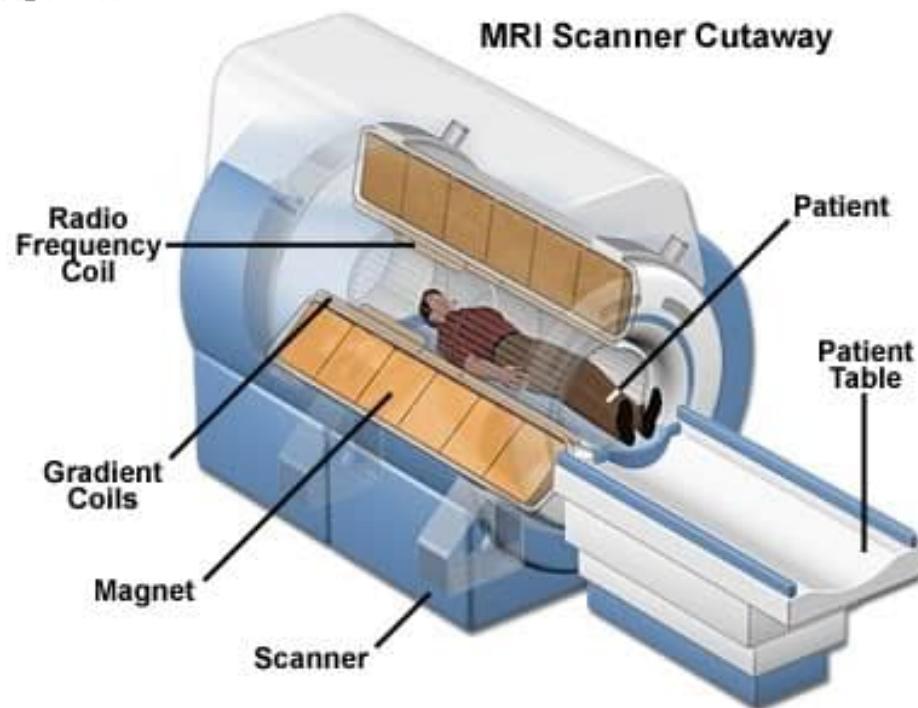
HTS (17 T), MgB_2 (5 T)



Electromagnet

Supplied loop current

Cu (2 T), HTS (> 30 T)



ITER: International Thermonuclear Experimental Reactor

since October, 2007

Cadarache,
France

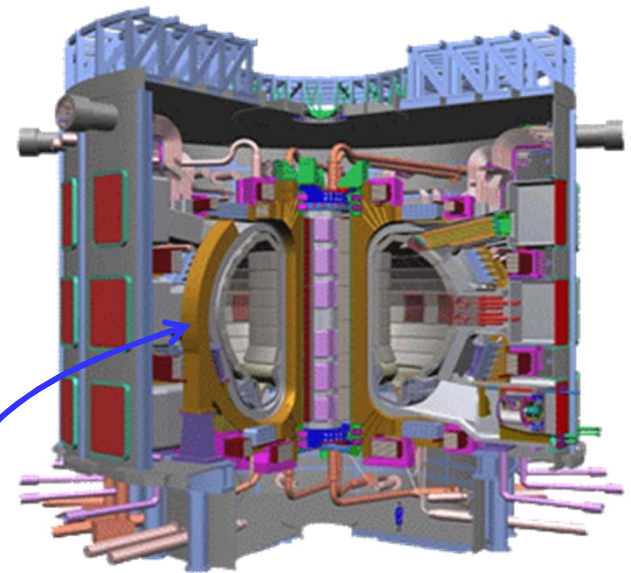
ITER
(予想図)

CEA Cadarache Laboratory

Nuclear Fusion
Reactor



NbTi or Nb₃Sn



Superconducting Magnets



Super-Maglev Train

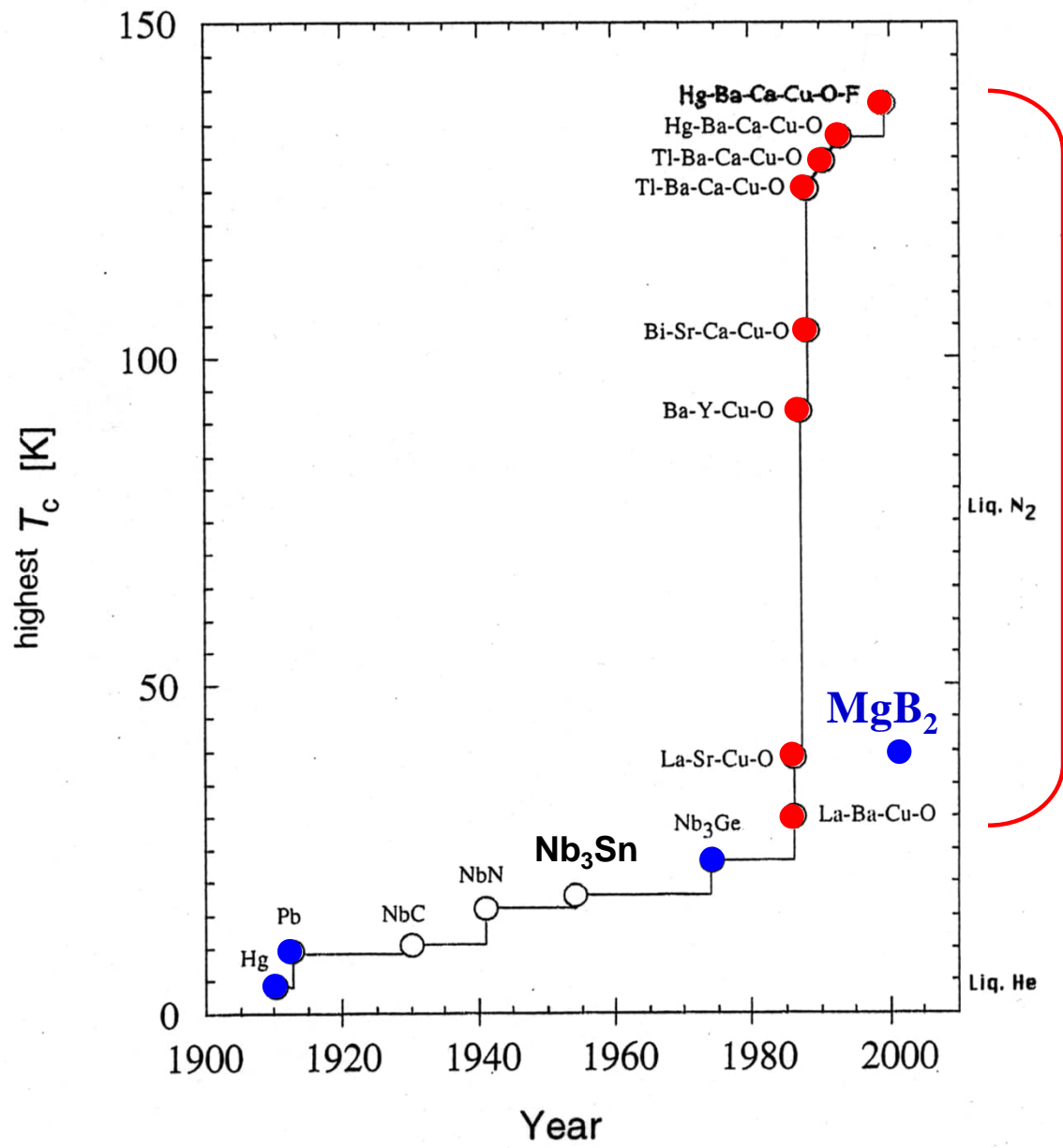
- 603 km / hour
- Test line 42.8 km

Superconducting Elements

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	Tl	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												

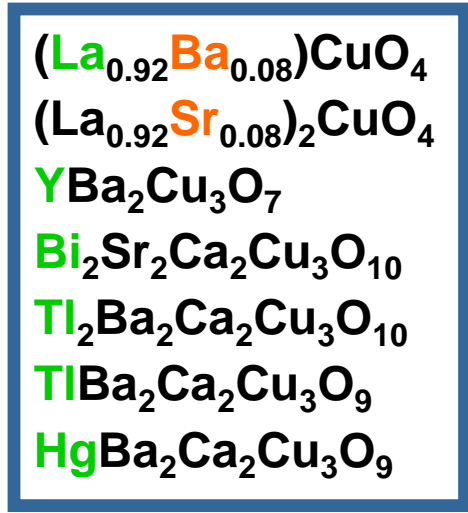
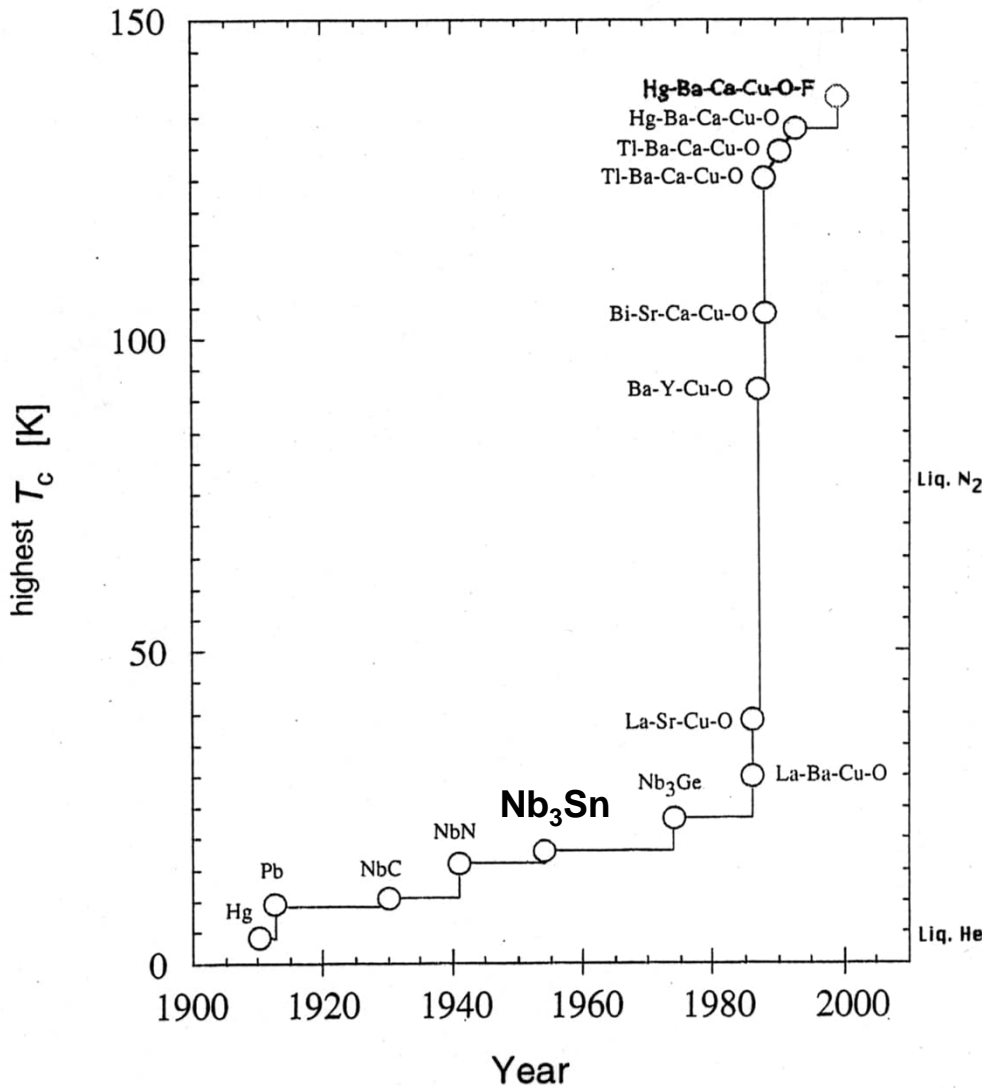
- In Bulk at Ambient Pressure
- At High Pressure
- In Modified Form

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cr	Es	Fm	Md	No	Lr



"HTSC"

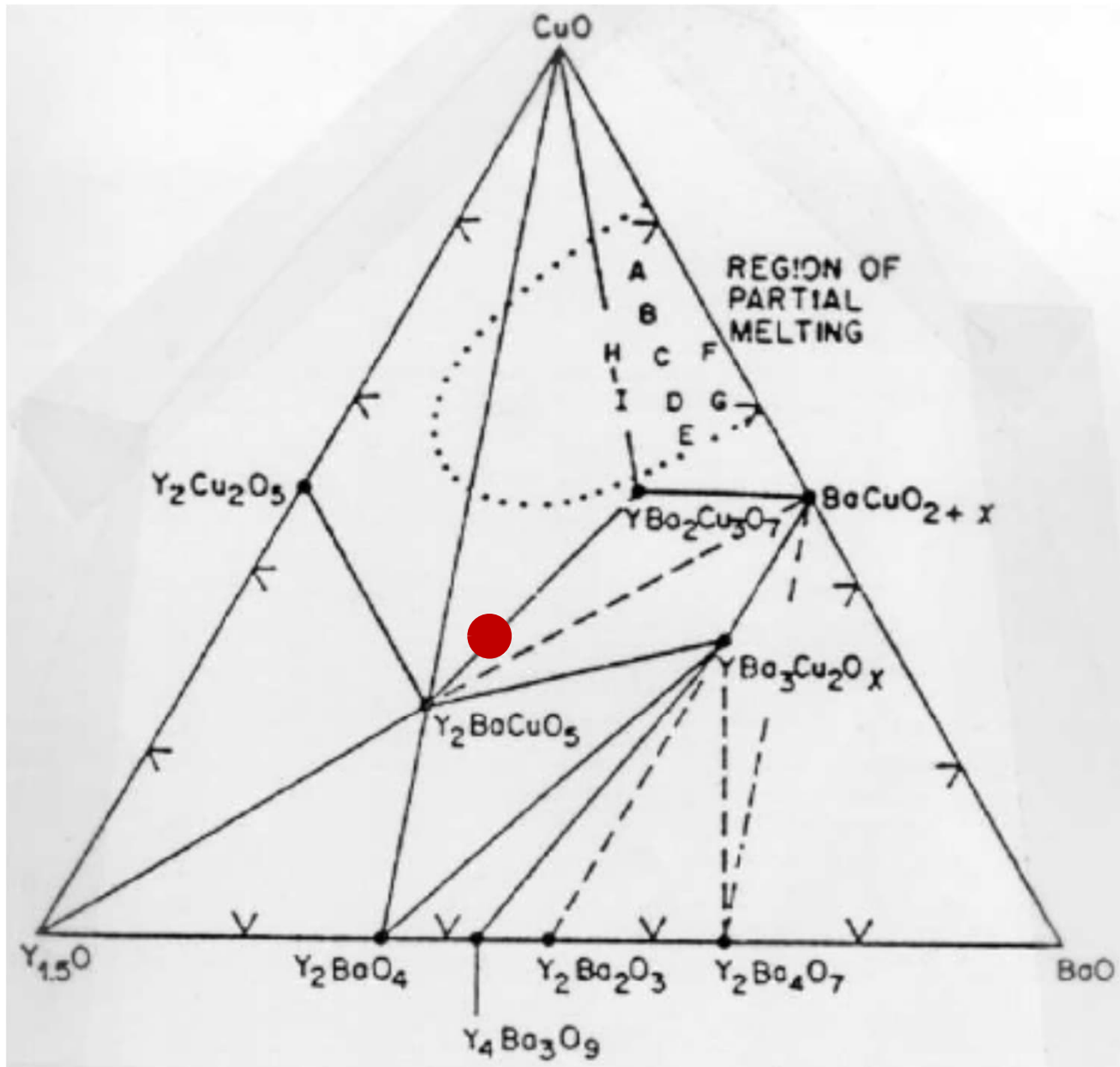
Search for new high- T_c superconductors

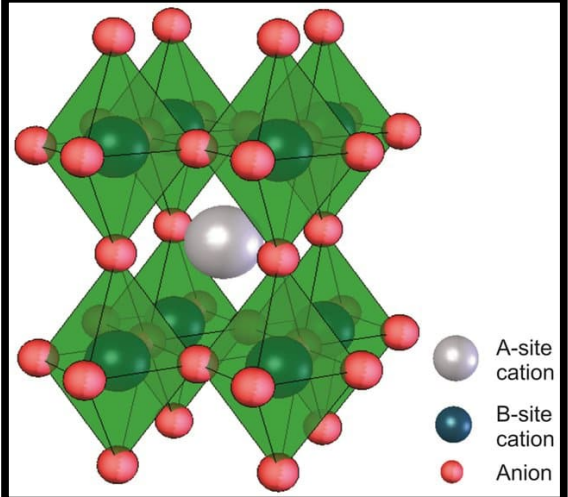


	IA																	VIIA or 0
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg	III B	IV B	V B	VIB	VII B	VIII B		IB	IIB	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 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 La to Lu	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 Ac to Lr	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 (0.5Y₂O₃-BaO-CuO): 1000°C, 1 atm O₂



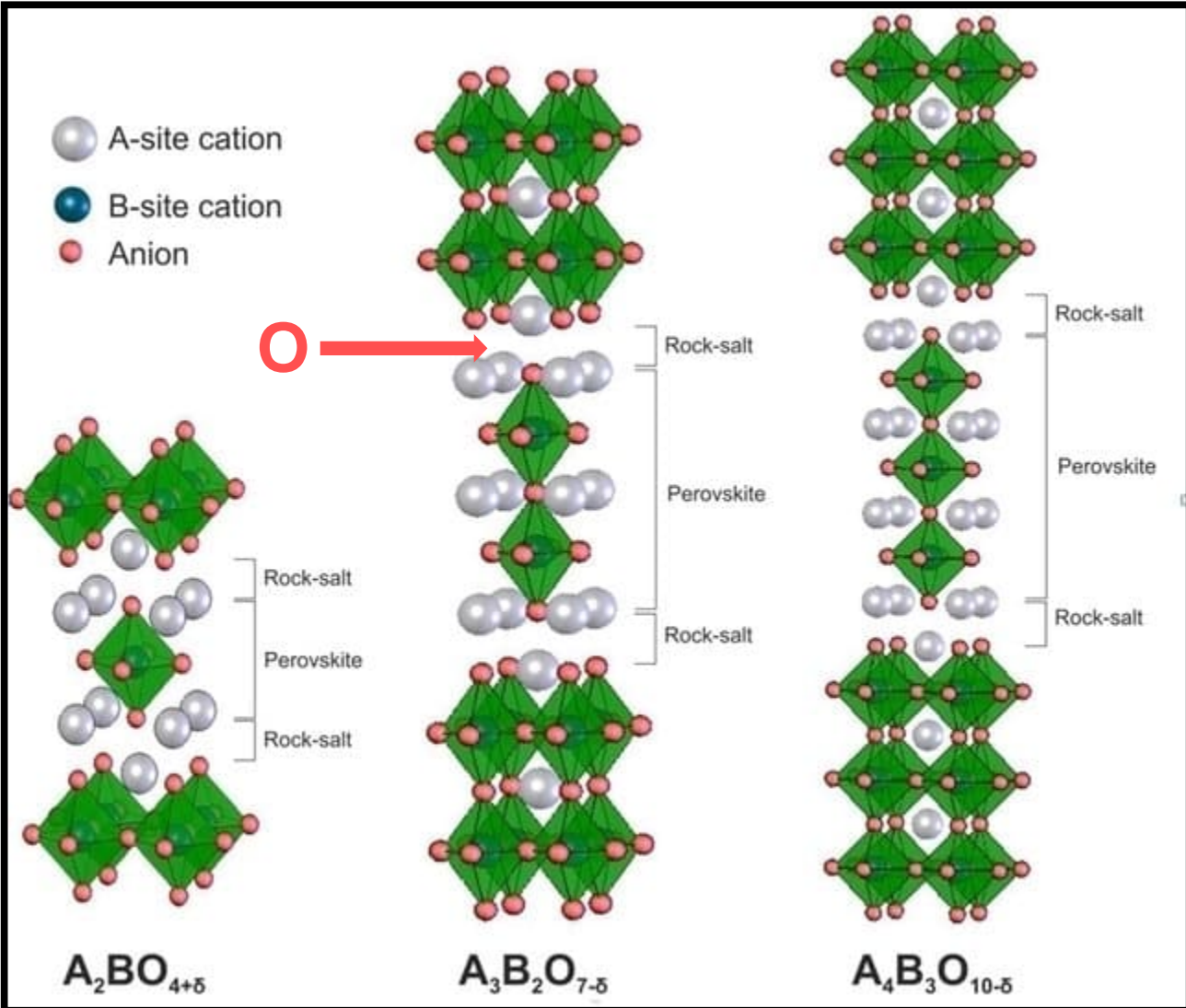


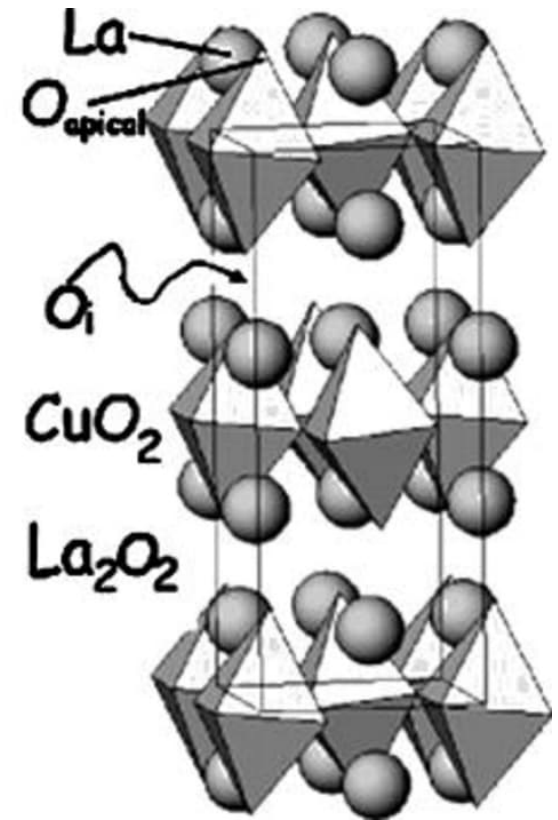
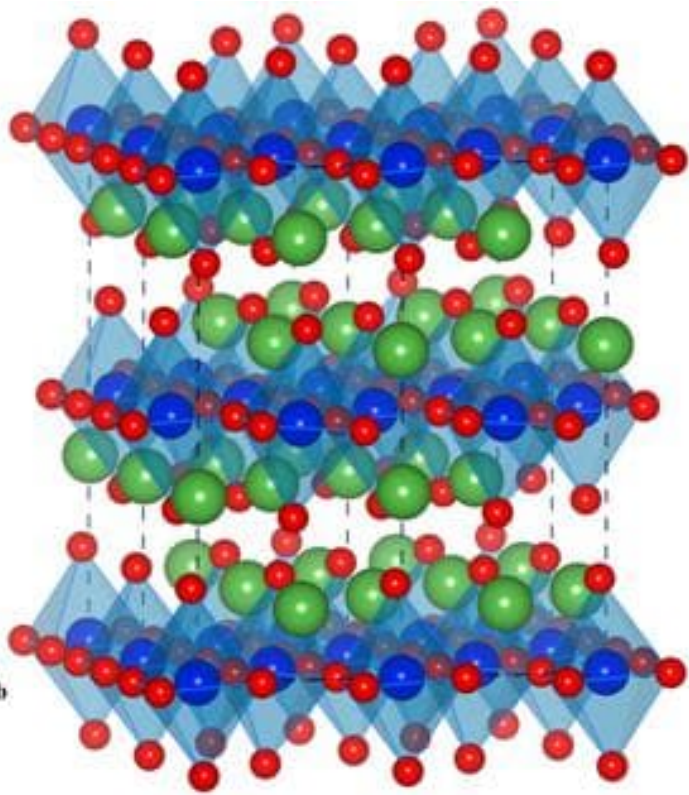
Perovskite ABO_3

- No space for interstitial oxygen

Ruddlesden-Popper $A_{n+1}B_nO_{1+3n}$

- Enough space for interstitial oxygen

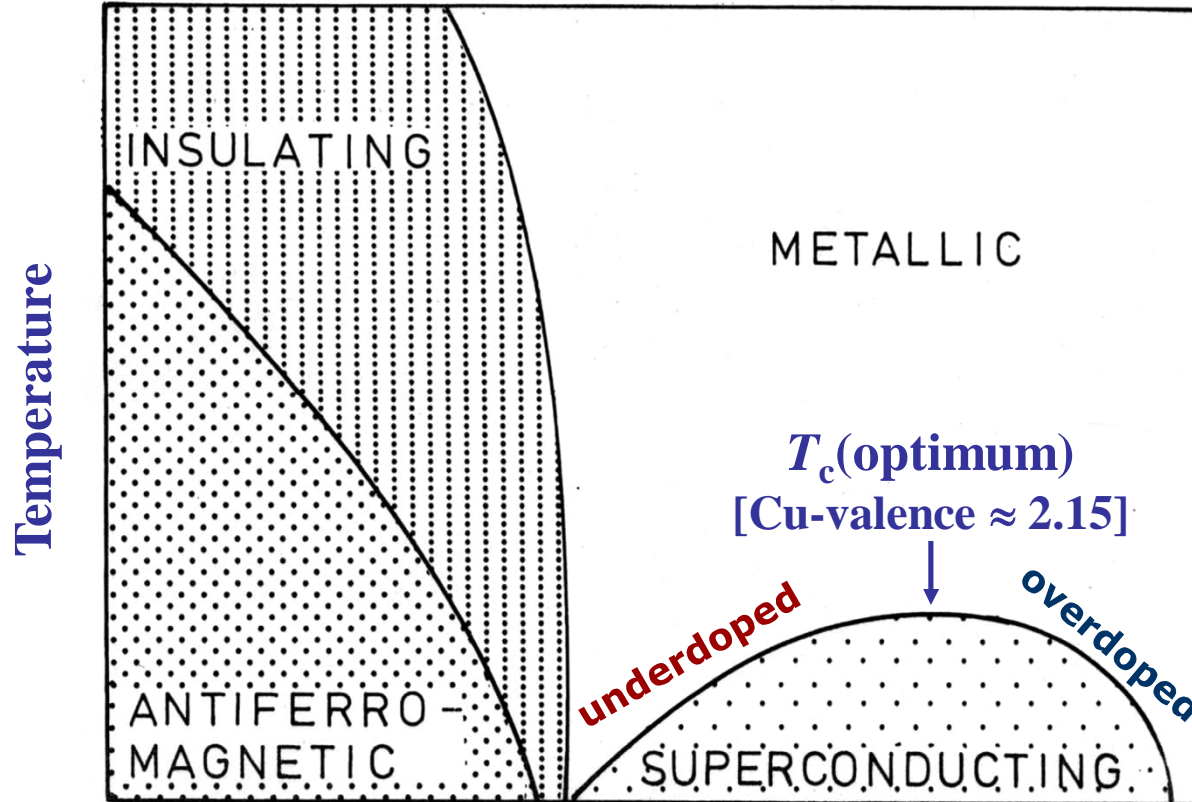




La₂CuO₄

- What is the copper valence in this compound ?
- Is this compound superconducting ?
- How to increase hole concentration ?

Phase Diagram of HTSCs

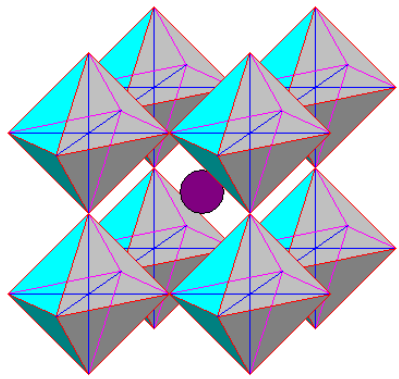


CuO₂-plane hole concentration [p(CuO₂)]
Valence of copper [V(Cu)]

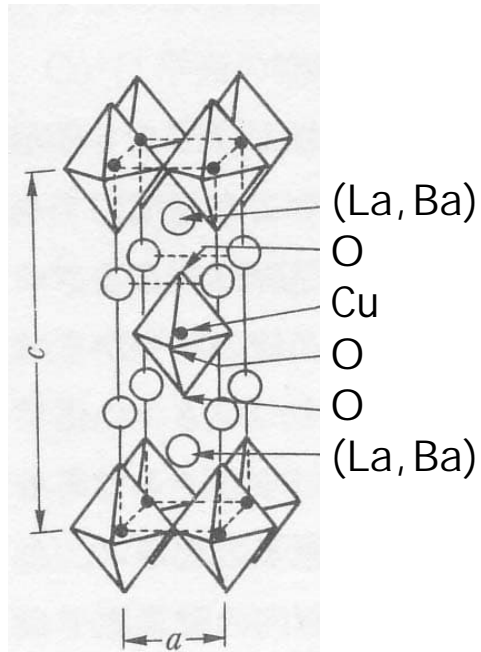
↑
Chemistry

Hole-carrier concentration
 $p(\text{CuO}_2) = V(\text{Cu}) - 2$

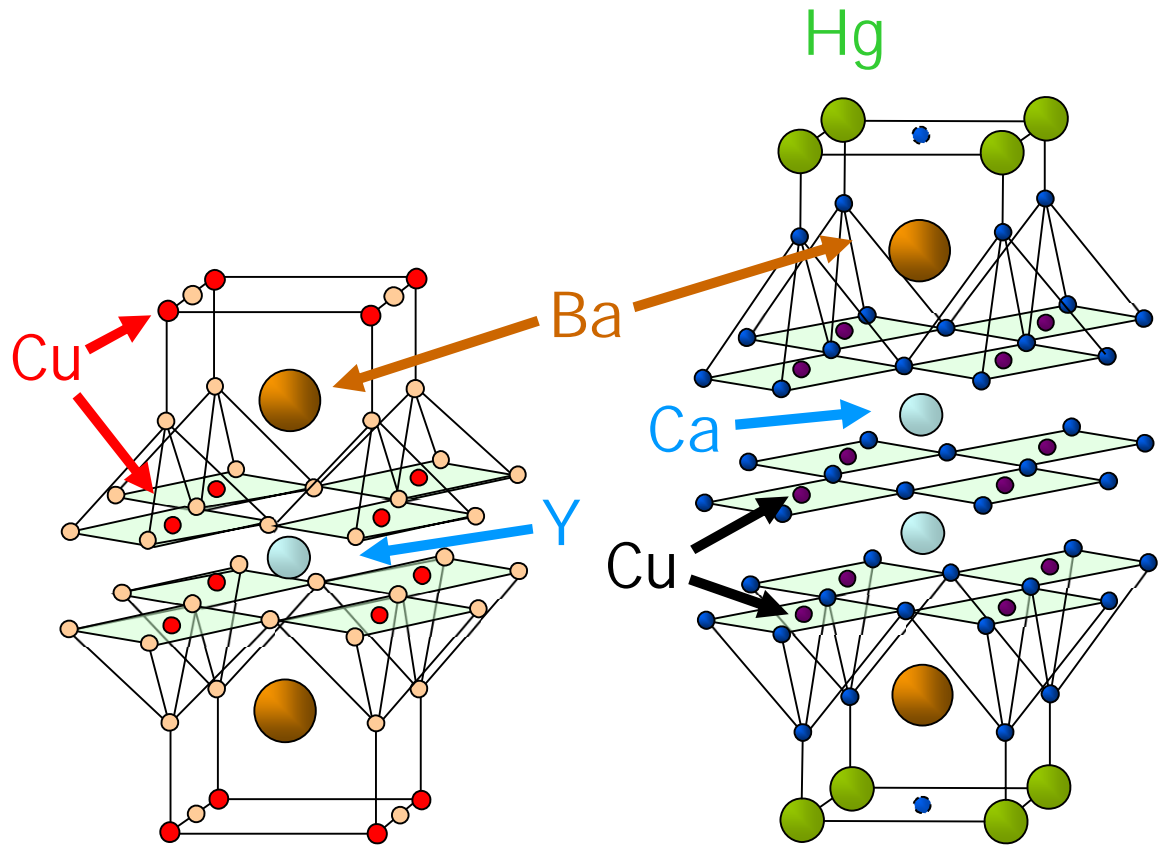
Crystal Structures of High- T_c Superconductive Copper Oxides



Perovskite CaTiO_3



$T_c \approx 35 \text{ K}$

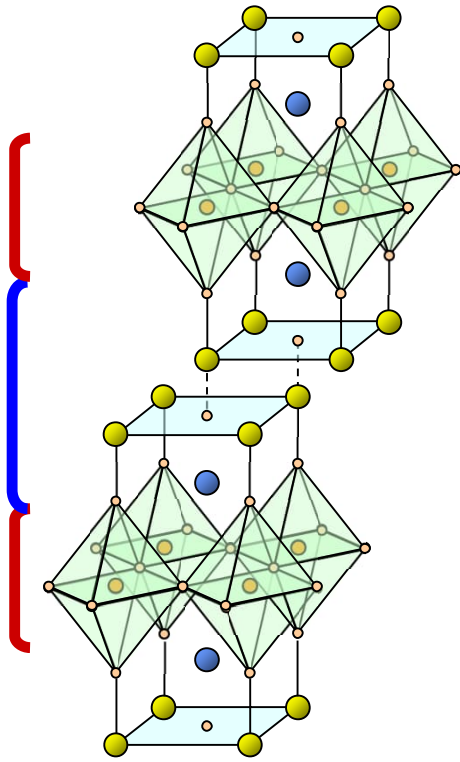


$T_c \approx 92 \text{ K}$

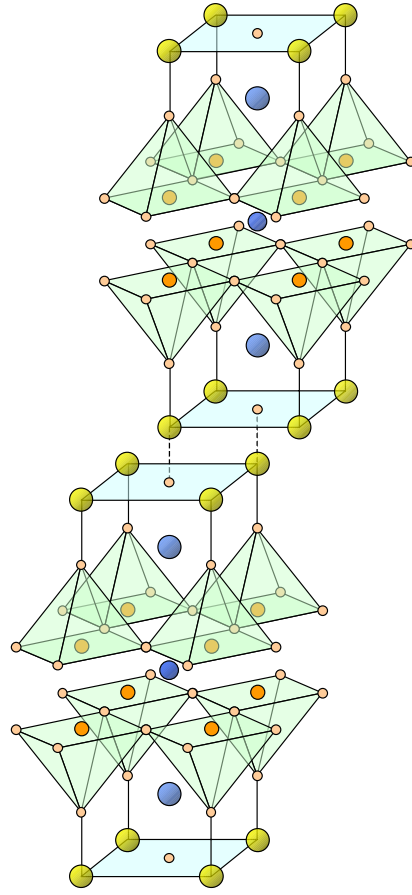


$T_c \approx 135 \text{ K}$

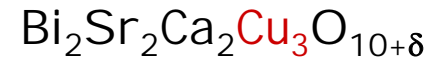
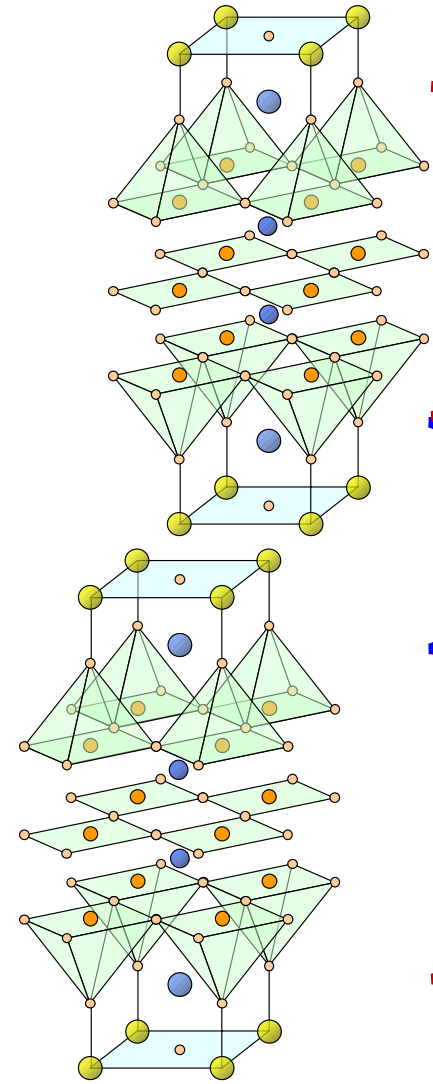
Homologous Series of Superconducting Copper Oxides



Bi-2201; $T_c \approx 20$ K



Bi-2212; $T_c \approx 80$ K

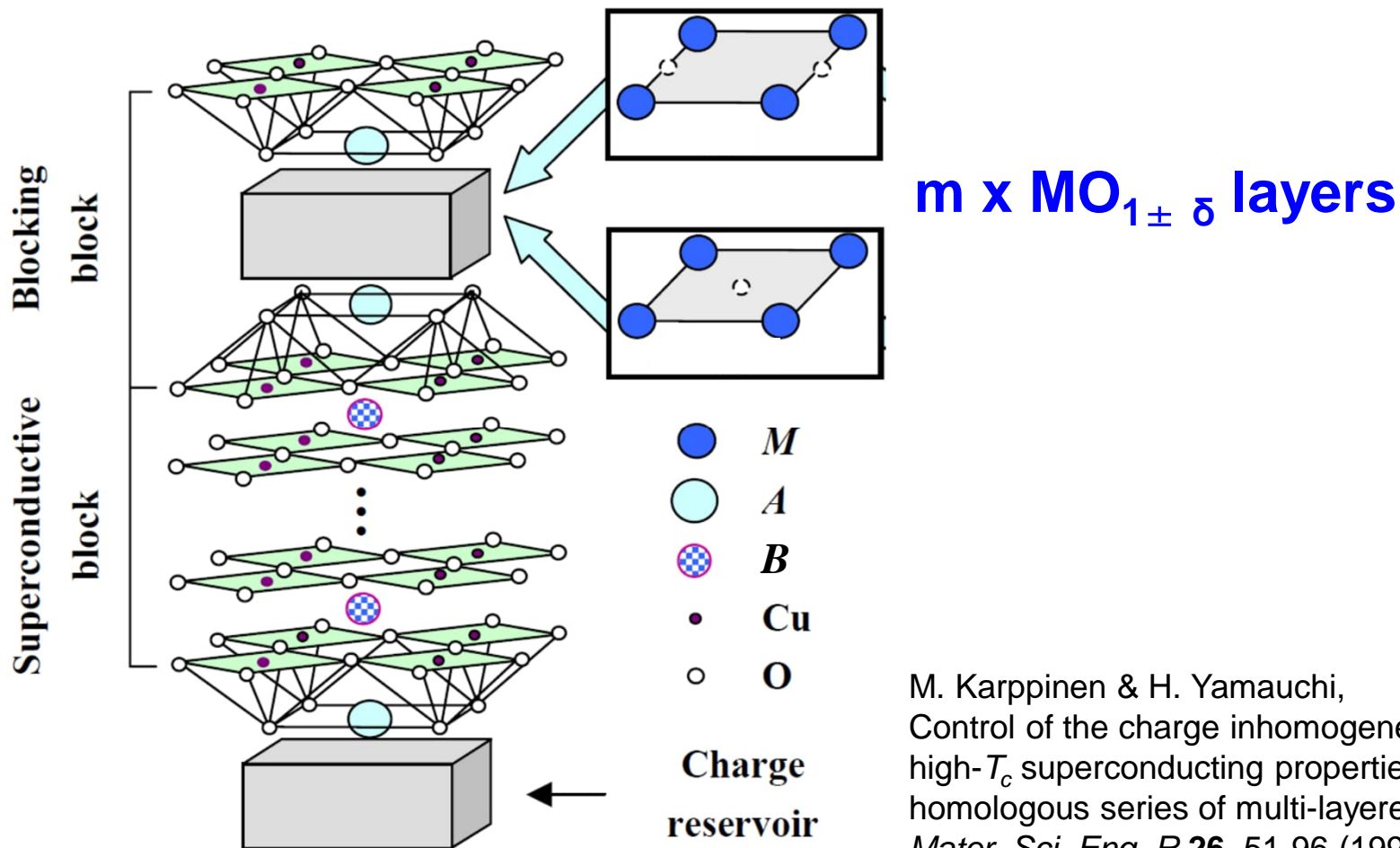


Bi-2223; $T_c \approx 110$ K

Superconducting Block
Blocking Block

GENERAL FORMULA

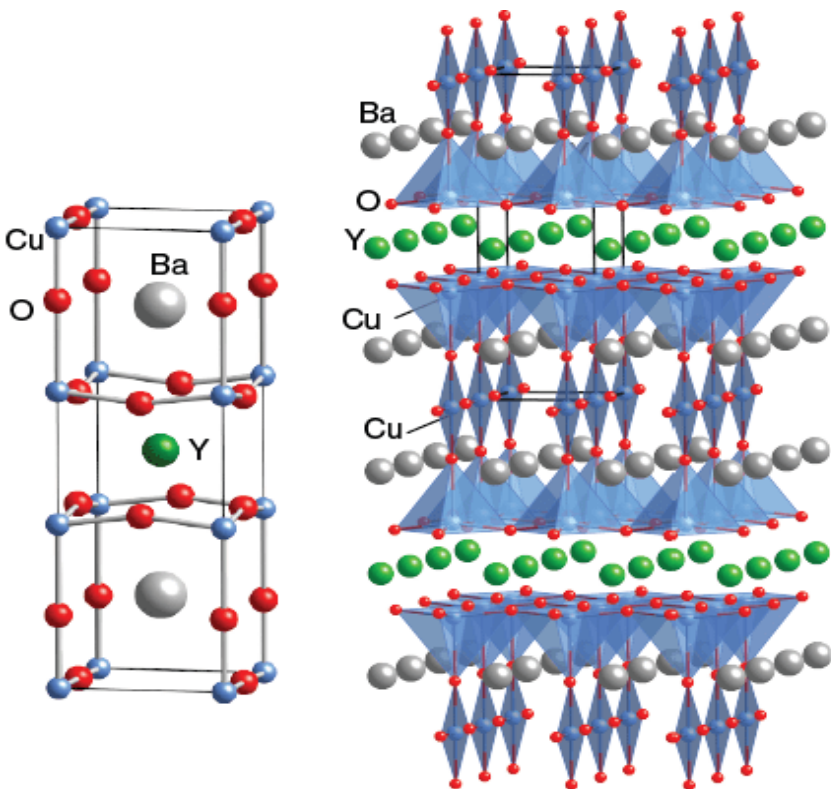
- $M_m A_2 B_{n-1} Cu_n O_{m+2+2n \pm \delta}$
- $M-m2(n-1)n$
- **HOMOLOGOUS SERIES:** M , m , A and B fixed, n varies



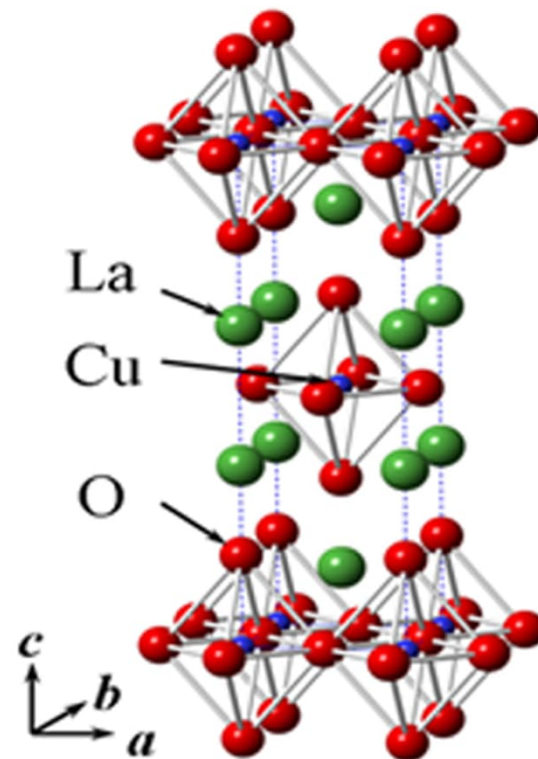
M. Karppinen & H. Yamauchi,
Control of the charge inhomogeneity and
high- T_c superconducting properties in
homologous series of multi-layered copper oxides,
Mater. Sci. Eng. R **26**, 51-96 (1999).

La₂CuO₄

- What is its M-m2(n-1)n type name ?



<https://www.chemtube3d.com/ss-yba2c3o7/>



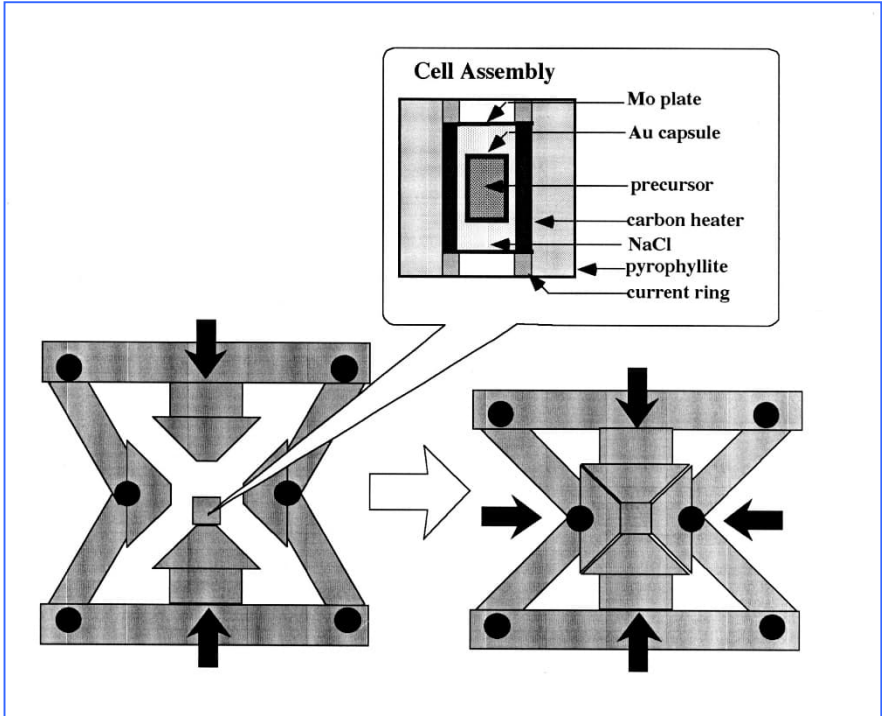
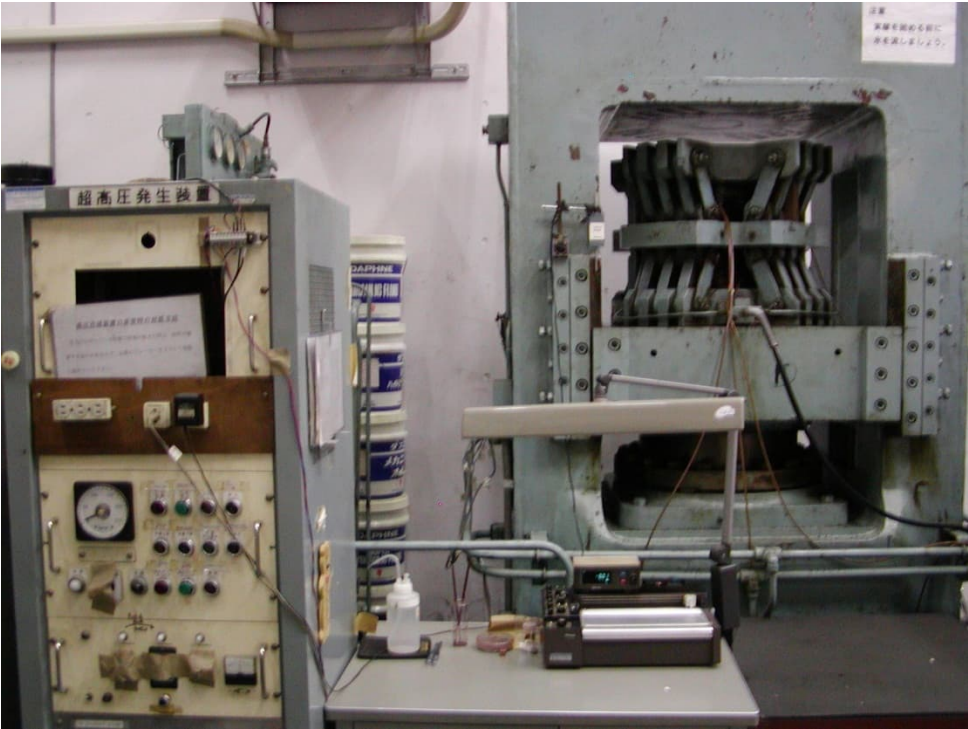
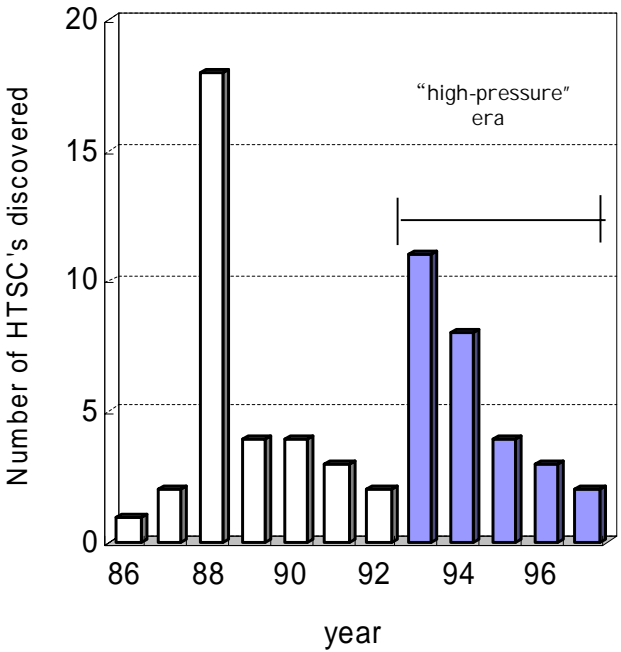
https://commons.wikimedia.org/wiki/File:La2CuO4_structure2.png

YBa₂Cu₃O_{7+d}

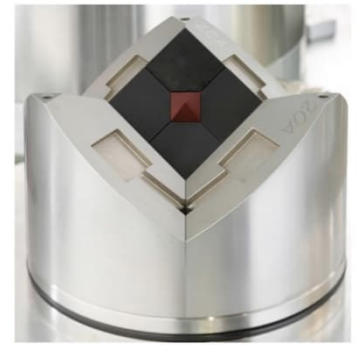
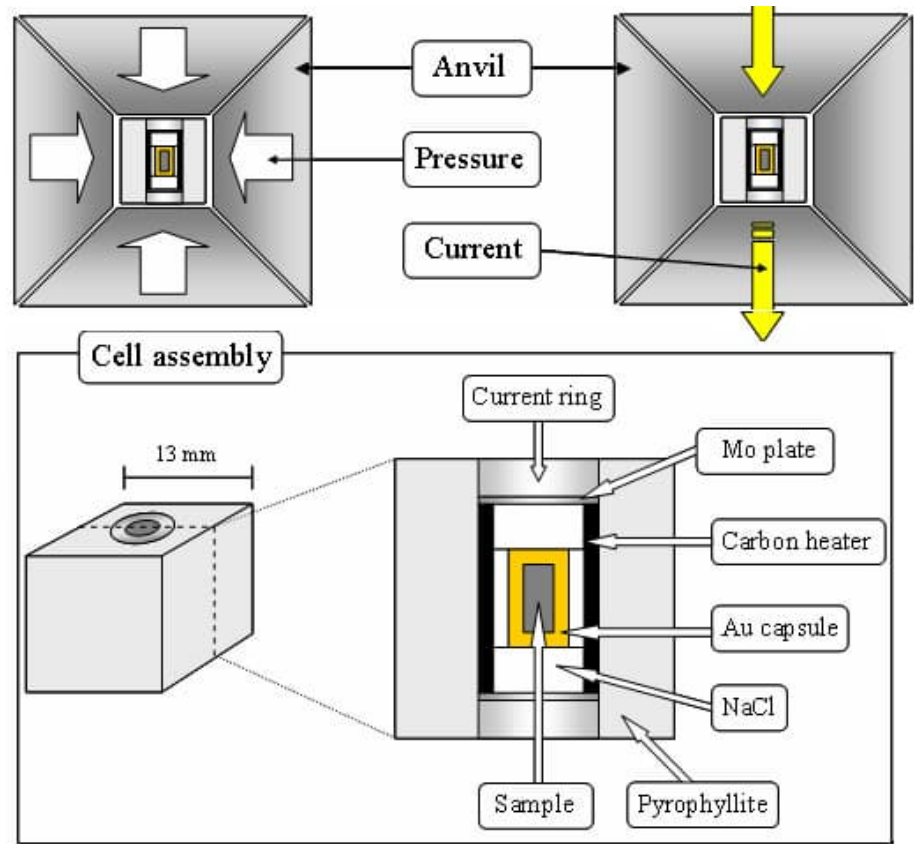
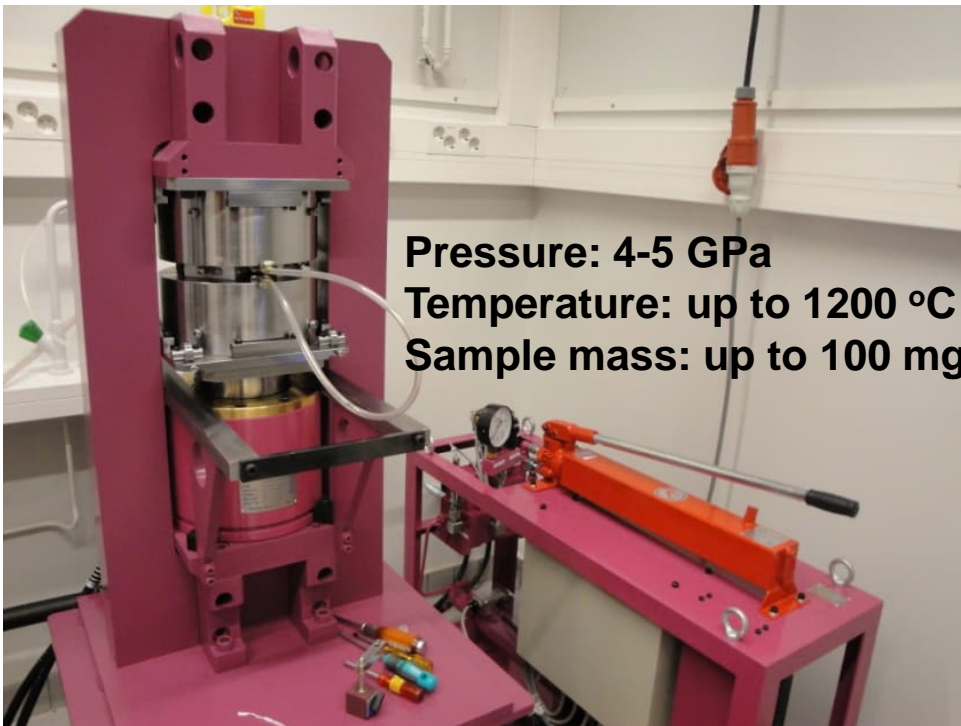
- M-m2(n-1)n type name ?
- Best way to write chemical formula ?

Ultra-High-Pressure Synthesis

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



OUR HIGH-PRESSURE EQUIPMENT



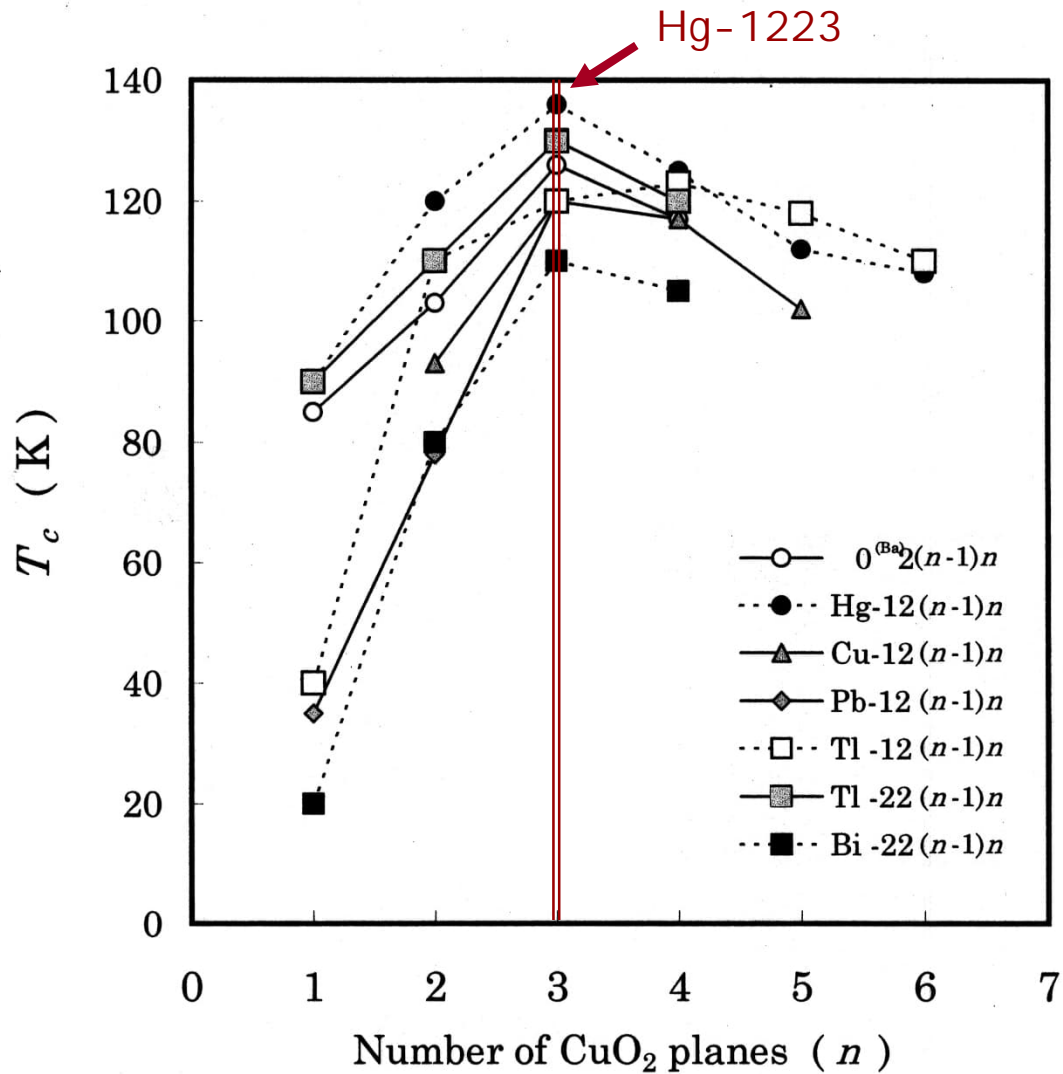


$$M - m2(n-1)n$$

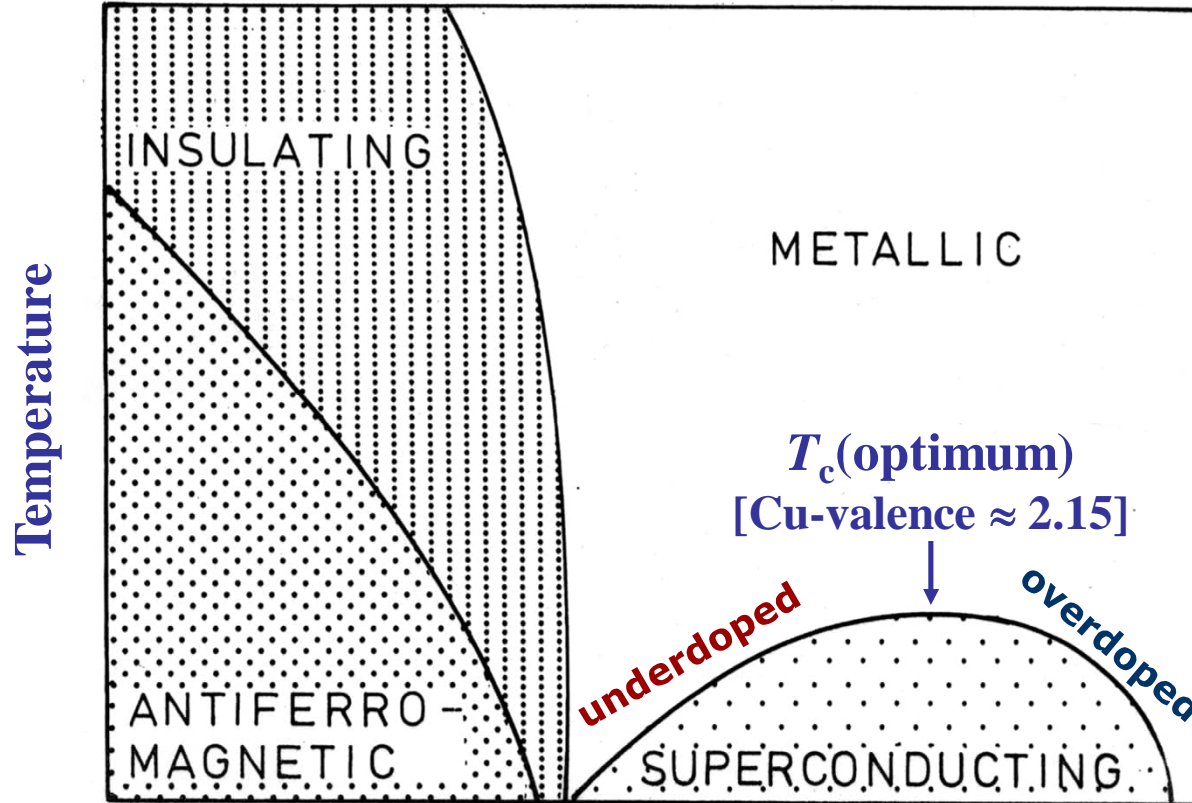
1 H																		2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag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



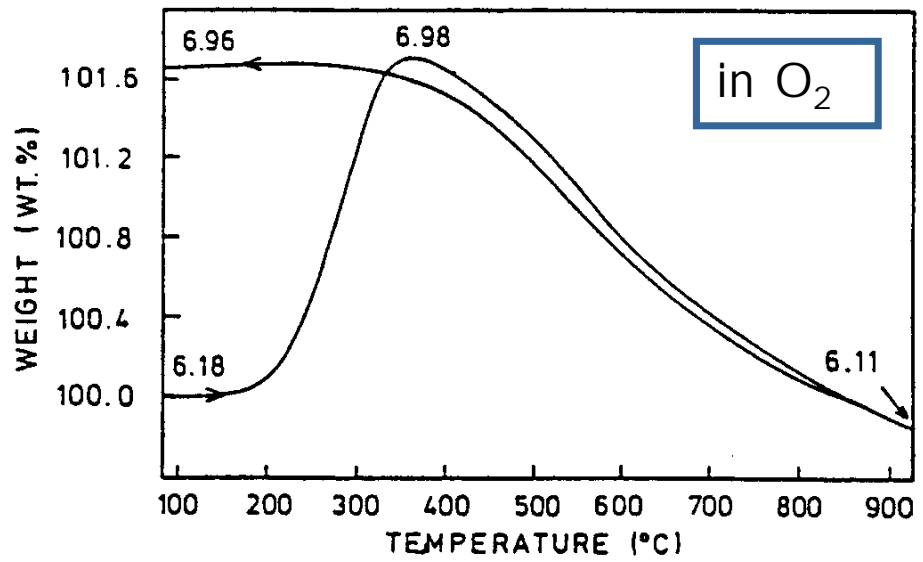
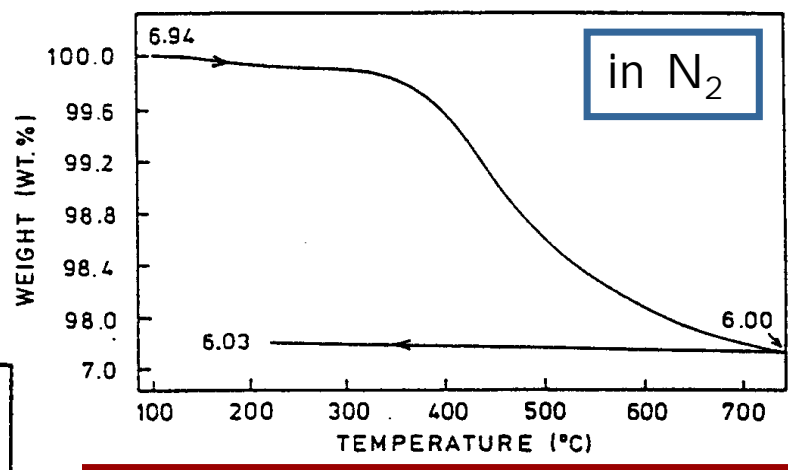
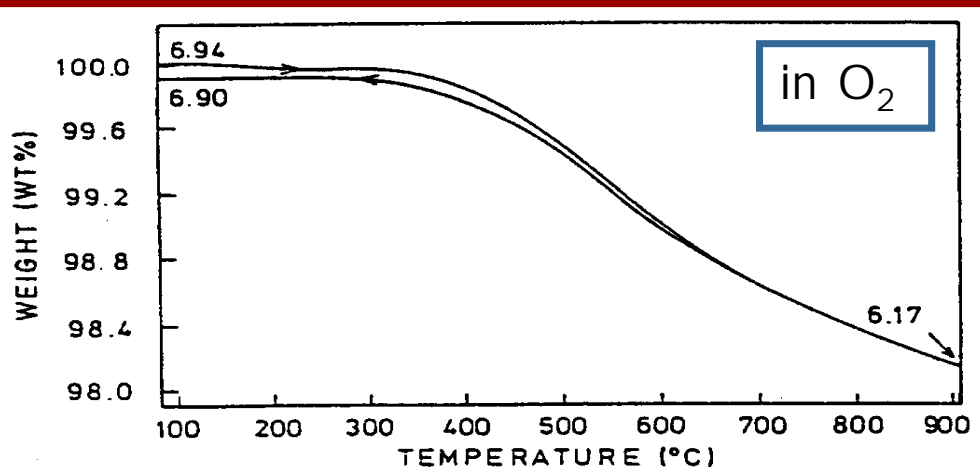
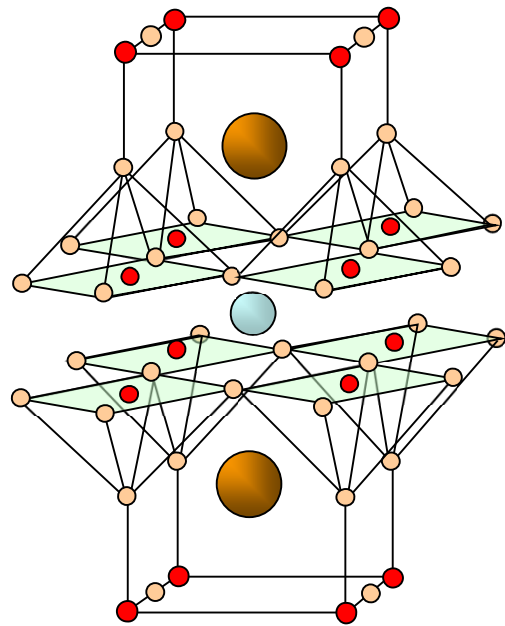
Phase Diagram of HTSC



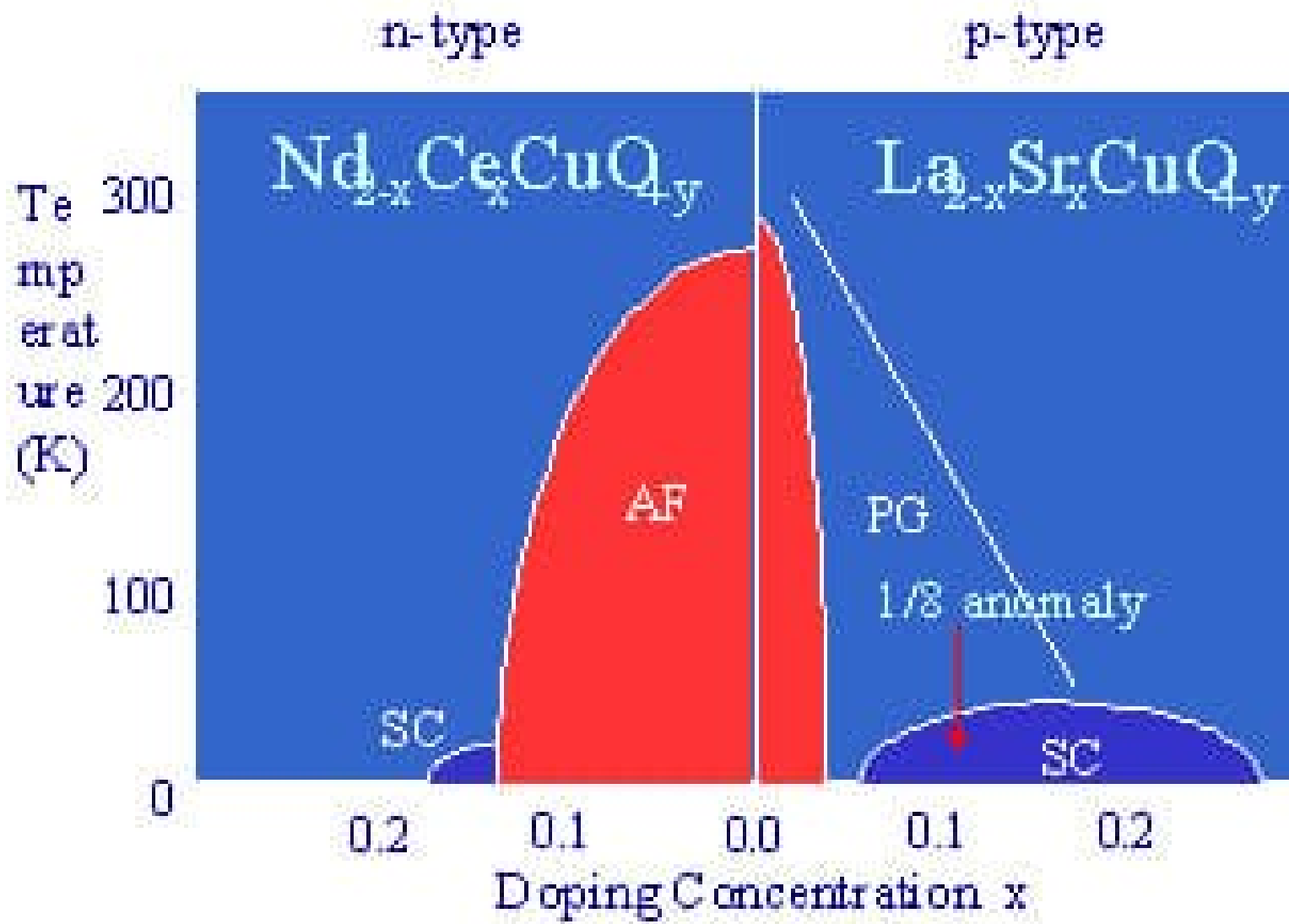
CuO_2 -plane hole concentration $[p(\text{CuO}_2)]$
Valence of copper $[V(\text{Cu})]$

↑
Chemistry

Hole-carrier concentration
 $p(\text{CuO}_2) = V(\text{Cu}) - 2$



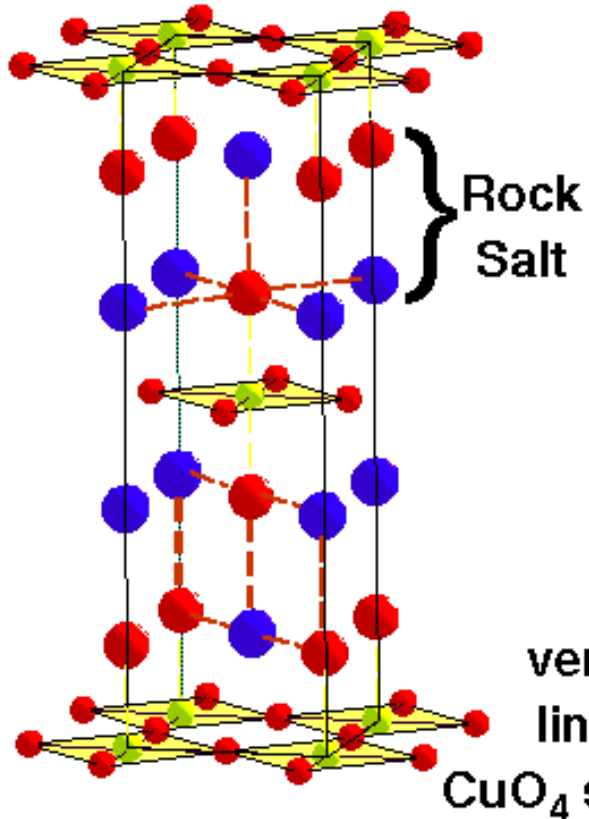
Created by [Serena Dai](#) and [Alice Gu](#), 2005. Updated October 2013 by [Yu Song](#).
 Currently managed by [Lebing Chen](#).



↑
 $V(\text{Cu}) = 2$

$n = \text{electron density} = 2 - V(\text{Cu})$
 $p = \text{hole density} = V(\text{Cu}) - 2$

p-type doping



n-type doping

