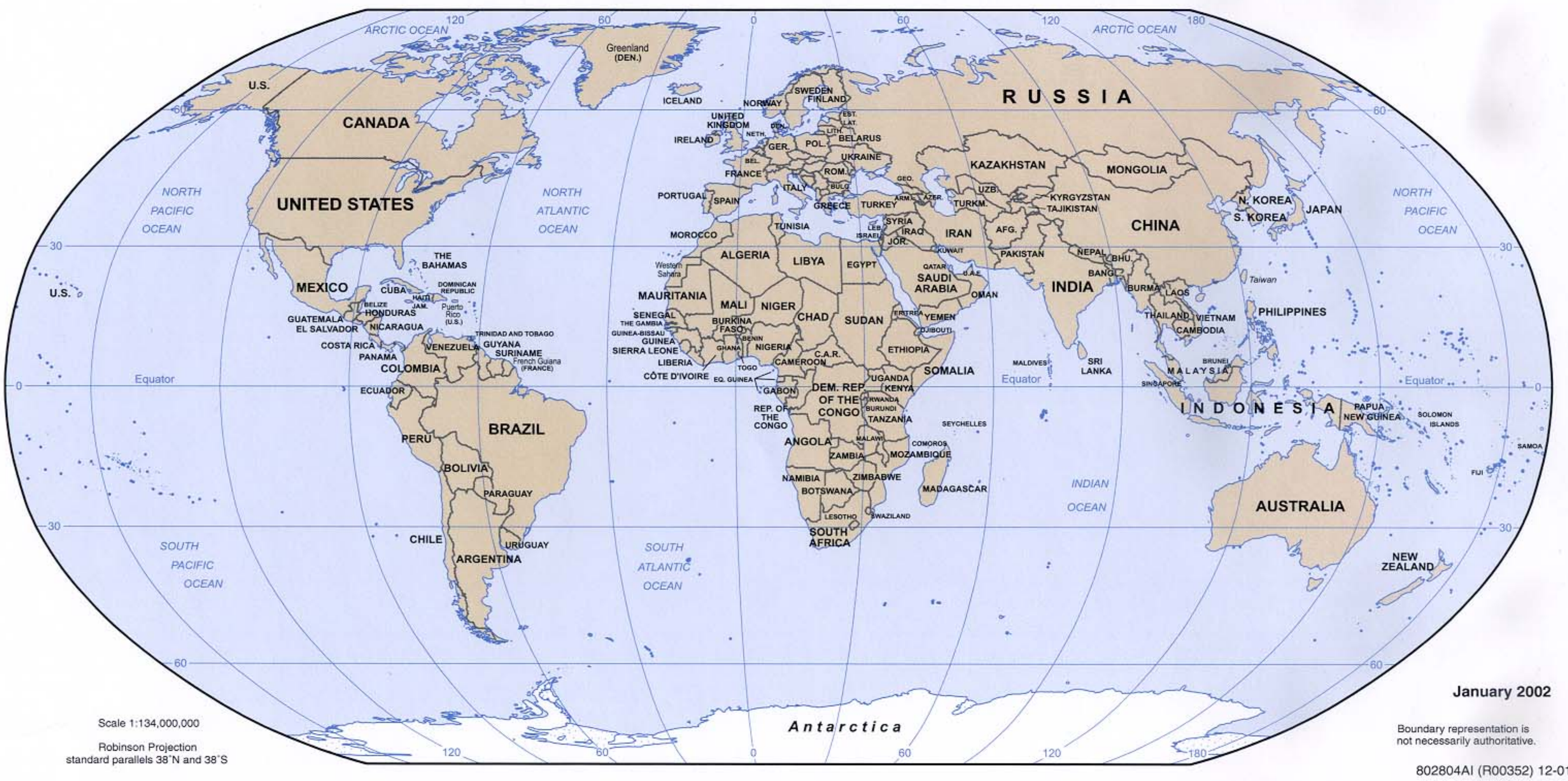
Santa Barbara, August 9, 2010

Correlated Oxides

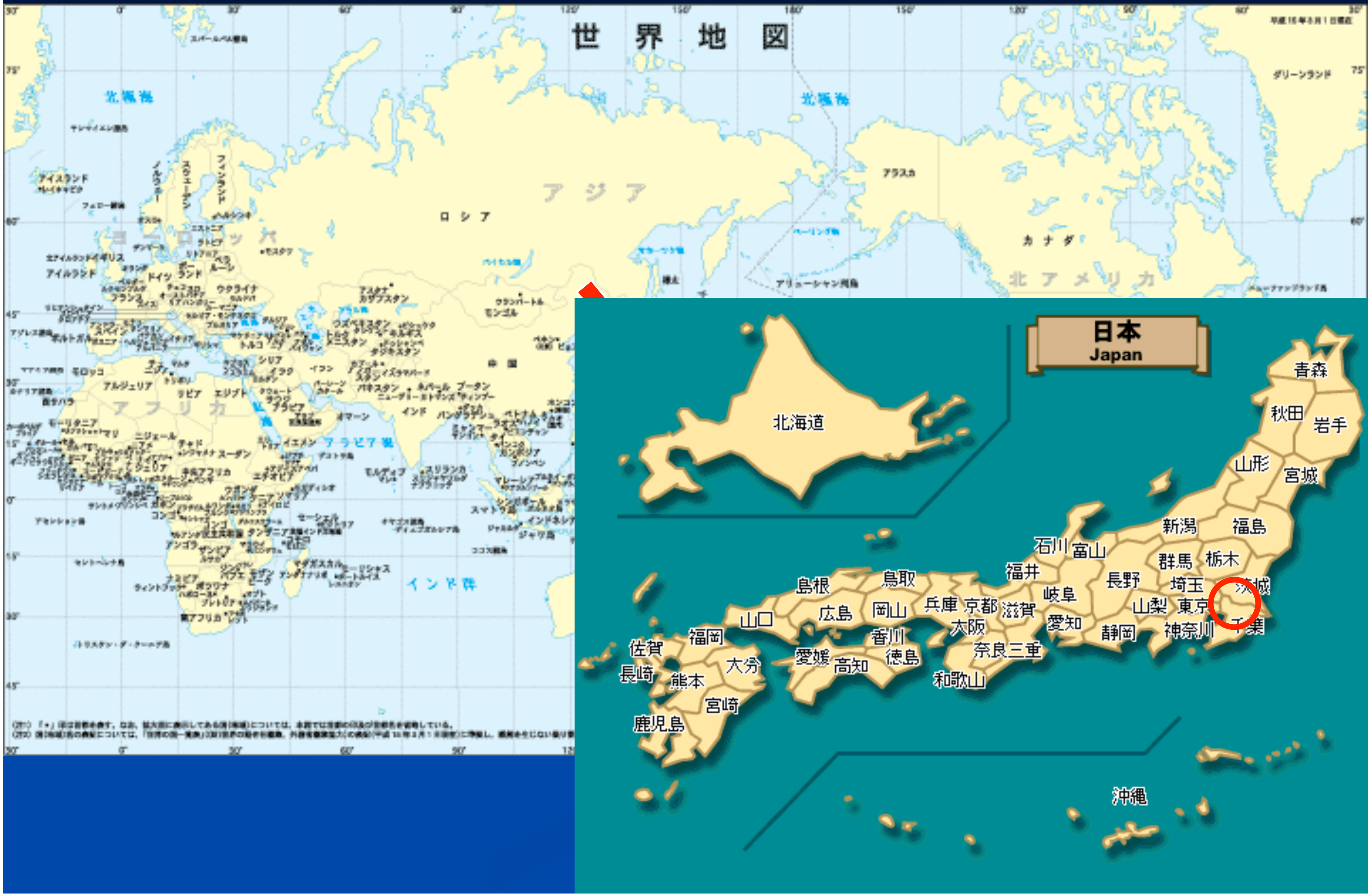
Zenji HIROI
ISSP, Univ. of Tokyo

World map 1



ARCTIC OCEAN
Greenland (DEN.)
ICELAND
U.S.
CANADA
UNITED STATES
NORTH PACIFIC OCEAN
NORTH ATLANTIC OCEAN
SOUTH PACIFIC OCEAN
SOUTH ATLANTIC OCEAN
INDIAN OCEAN
MEXICO
CUBA
THE BAHAMAS
DOMINICAN REPUBLIC
HAITI
JAM.
Puerto Rico (U.S.)
BELIZE
HONDURAS
GUATEMALA
EL SALVADOR
NICARAGUA
COSTA RICA
PANAMA
TRINIDAD AND TOBAGO
VENEZUELA
GUYANA
SURINAME
French Guiana (FRANCE)
COLOMBIA
ECUADOR
PERU
BRAZIL
BOLIVIA
PARAGUAY
CHILE
ARGENTINA
URUGUAY
NORWAY
SWEDEN
FINLAND
UNITED KINGDOM
IRELAND
EST.
LAT.
LITH.
BELARUS
NETH.
GER.
POL.
BEL.
UKRAINE
FRANCE
ROM.
BULG.
PORTUGAL
SPAIN
ITALY
GREECE
TURKEY
GEO.
ARM.
AZER.
RUSSIA
KAZAKHSTAN
MONGOLIA
UZB.
TURKM.
KYRGYZSTAN
TAJIKISTAN
AFG.
N. KOREA
S. KOREA
JAPAN
CHINA
MOROCCO
TUNISIA
ALGERIA
LIBYA
EGYPT
Western Sahara
MAURITANIA
MALI
NIGER
CHAD
SUDAN
SENEGAL
THE GAMBIA
GUINEA-BISSAU
GUINEA
SIERRA LEONE
LIBERIA
CÔTE D'IVOIRE
BURKINA FASO
GHANA
TOGO
BENIN
NIGERIA
CAMEROON
EQ. GUINEA
GABON
C.A.R.
REP. OF THE CONGO
DEM. REP. OF THE CONGO
ETHIOPIA
ERITREA
DJIBOUTI
SOMALIA
UGANDA
KENYA
RWANDA
BURUNDI
TANZANIA
ANGOLA
ZAMBIA
MALAWI
MOZAMBIQUE
COMOROS
SEYCHELLES
NAMIBIA
ZIMBABWE
BOTSWANA
MADAGASCAR
LESOTHO
SWAZILAND
SOUTH AFRICA
SYRIA
LEB.
ISRAEL
IRAQ
JOR.
IRAN
KUWAIT
QATAR
U.A.E.
SAUDI ARABIA
OMAN
YEMEN
PAKISTAN
INDIA
NEPAL
BHU.
BANG.
MALDIVES
SRI LANKA
BURMA
LAOS
THAILAND
VIETNAM
CAMBODIA
Taiwan
PHILIPPINES
BRUNEI
MALAYSIA
SINGAPORE
INDONESIA
PAPUA NEW GUINEA
SOLOMON ISLANDS
SAMOA
FIJI
AUSTRALIA
NEW ZEALAND
Antarctica
Equator
January 2002
Scale 1:134,000,000
Robinson Projection
standard parallels 38°N and 38°S
Boundary representation is
not necessarily authoritative.
802804AI (R00352) 12-01

World map 2



世 界 地 図
ア ジ ア
ロ シ ア
カ ナ ダ
北 ア メ リ カ
ア フ リ カ
イ ン ド 洋
日本
Japan
北海道
青森
秋田
岩手
山形
宮城
新潟
福島
石川
富山
群馬
栃木
福井
長野
埼玉
島根
鳥取
岐阜
山梨
東京
山口
広島
岡山
兵庫
京都
滋賀
大阪
愛知
静岡
神奈川
佐賀
福岡
香川
奈良
三重
大分
愛媛
高知
徳島
長崎
熊本
和歌山
宮崎
鹿児島
沖縄

物性研究所

Institute for Solid State Physics
ISSP

東京大学

University of Tokyo

Santa Barbara, August 9, 2010

Correlated Oxides

Zenji HIROI

Materials Design and Characterization Lab

Institute for Solid State Physics

University of Tokyo

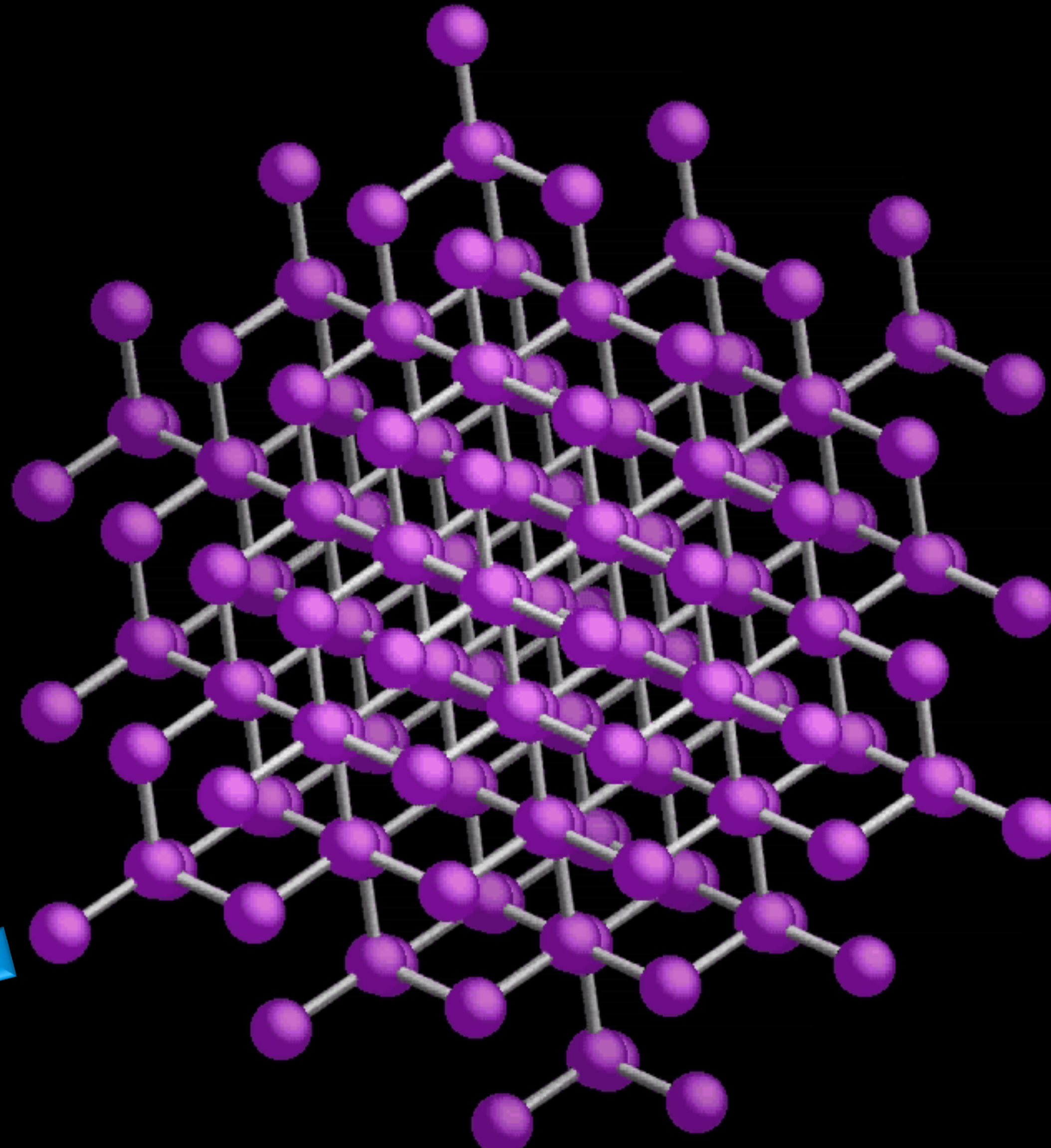
Staff	Yoshihiko Okamoto, Jun-Ichi Yamaura
PD	Yui Ishii, (Goran Nilsen)
Students	Takashi Shimizu, Atsushi Onosaka



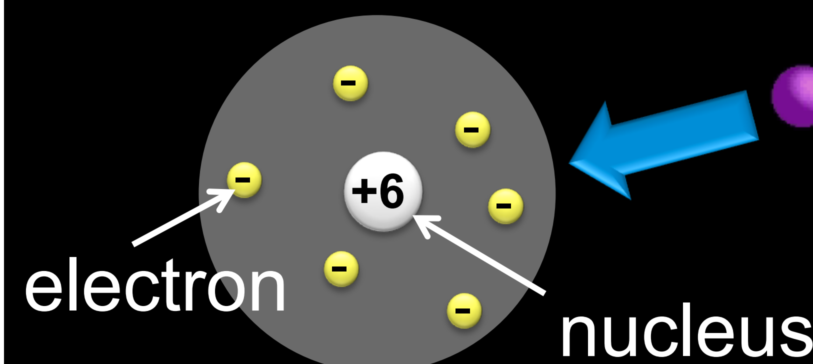


Diamond

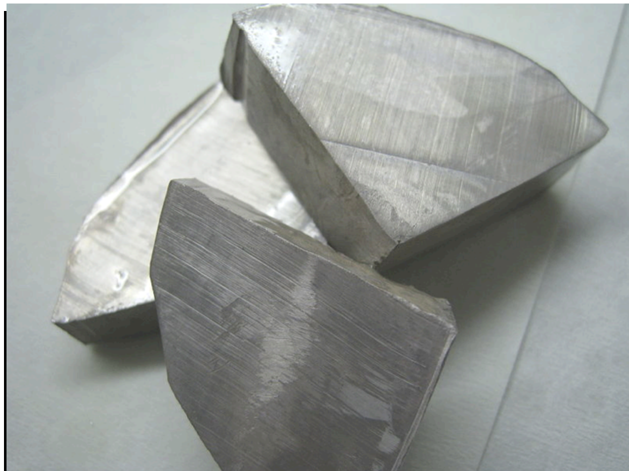
Millennium star
（De Beers）203 ct



Carbon atom

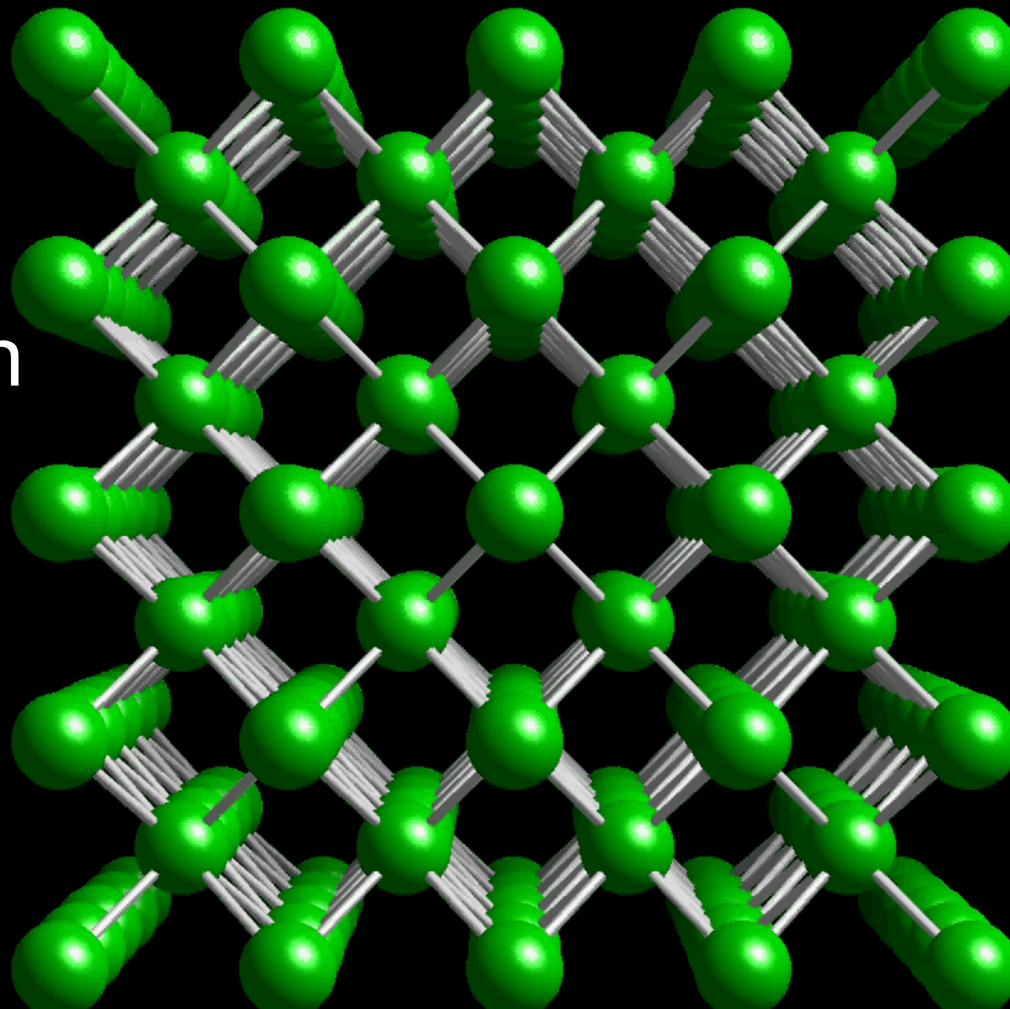


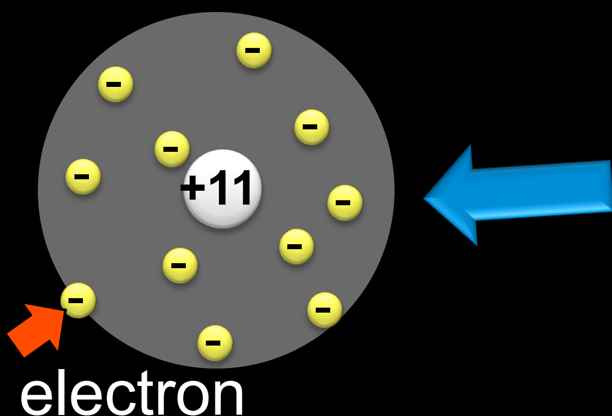
Sodium



Sodium crystal

“free”electron





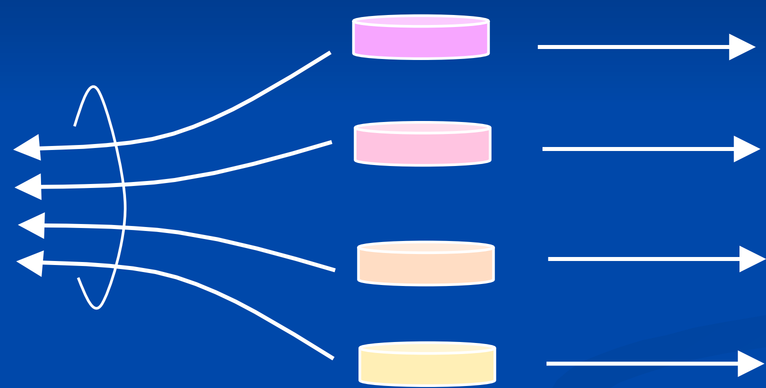
Na atom

Materials Science 物質科学

Novel phenomena | **New compounds**

Properties: conductivity, magnetism, dielectric, thermoelectric, ...

Organizing principle



Samples

Individuals
Empirical
Systematics

Physics

Understanding of underlying discipline

Chemistry

Understanding of each material

"Modern science is the search for new organizing principles of nature."
by R. B. Laughlin (1998 Novel prize) at Kashiwa, 2001

Strategy for new materials

Physics vs. Chemistry

Physics	Chemistry
“exact”	serious
analytical	optimistic
“about”	dreaming

the outcome limited

Some approximations necessary

often complicated and sometimes wired!

Active conversations are required.

Strategy for new materials

Design vs. Serendipity

Which topics or materials should we study?

Following the fashion, or going my way?

stimulated by a theoretical prediction?

From crystal structures to desired systems.
However, appearances are often deceptive.
Real materials always suffer from various obstacles.

Strategy for new materials

Physics	vs.	Chemistry
Design	vs.	Serendipity

Nature often complicated, but fascinating!

We should keep a humble attitude toward nature.

When I observe something predicted by theory,
it's OK but not so exciting.

When I observe something unexpected,
I would be more happy.

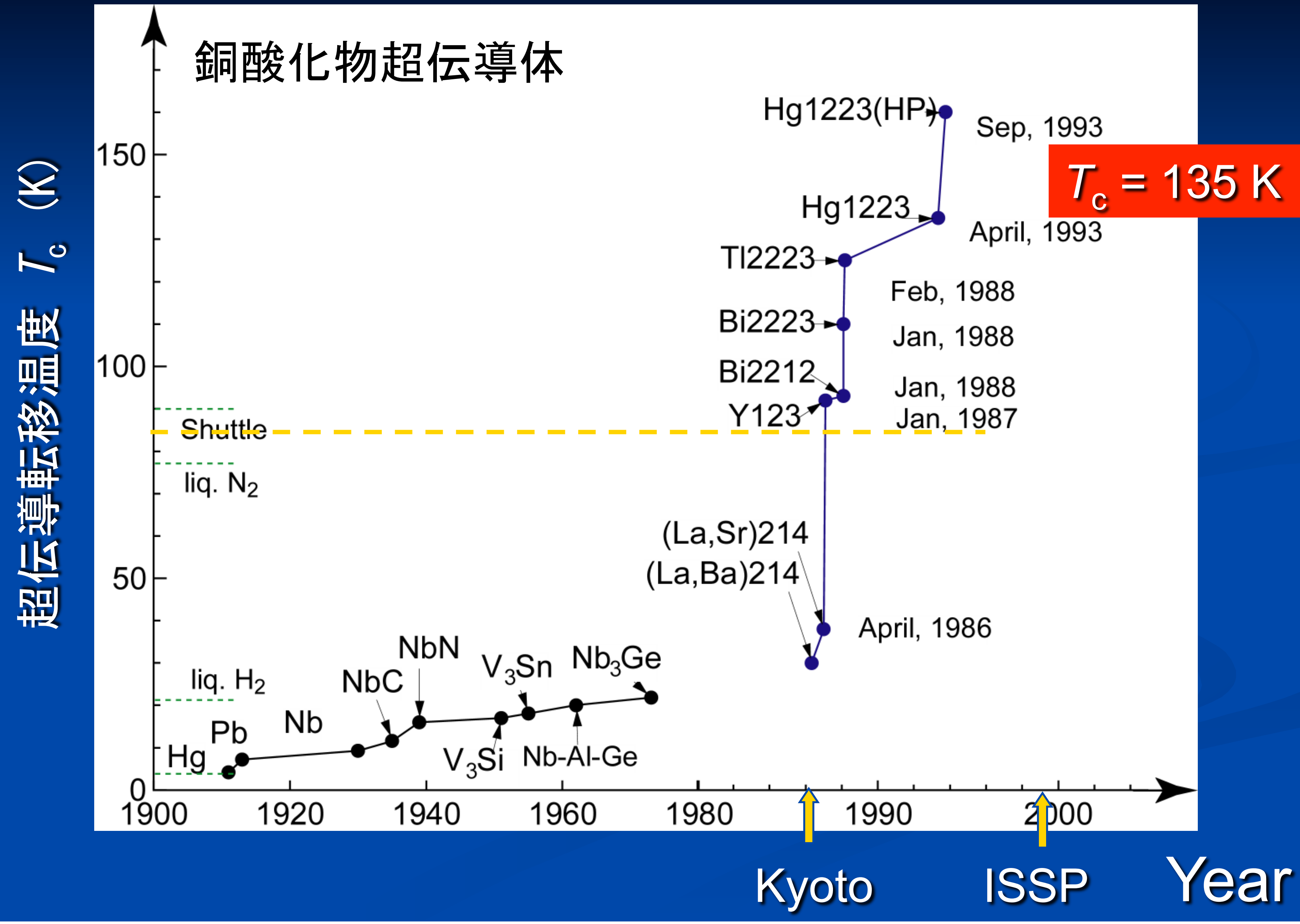
Motivation of our research

New materials with novel properties

Transition metal oxides with strongly correlated electrons

Superconductivity,
Magnetism, or
Other exotic phenomena

High-Temperature Superconductors



Correlated Oxides:

I. A road to a room-temperature superconductor

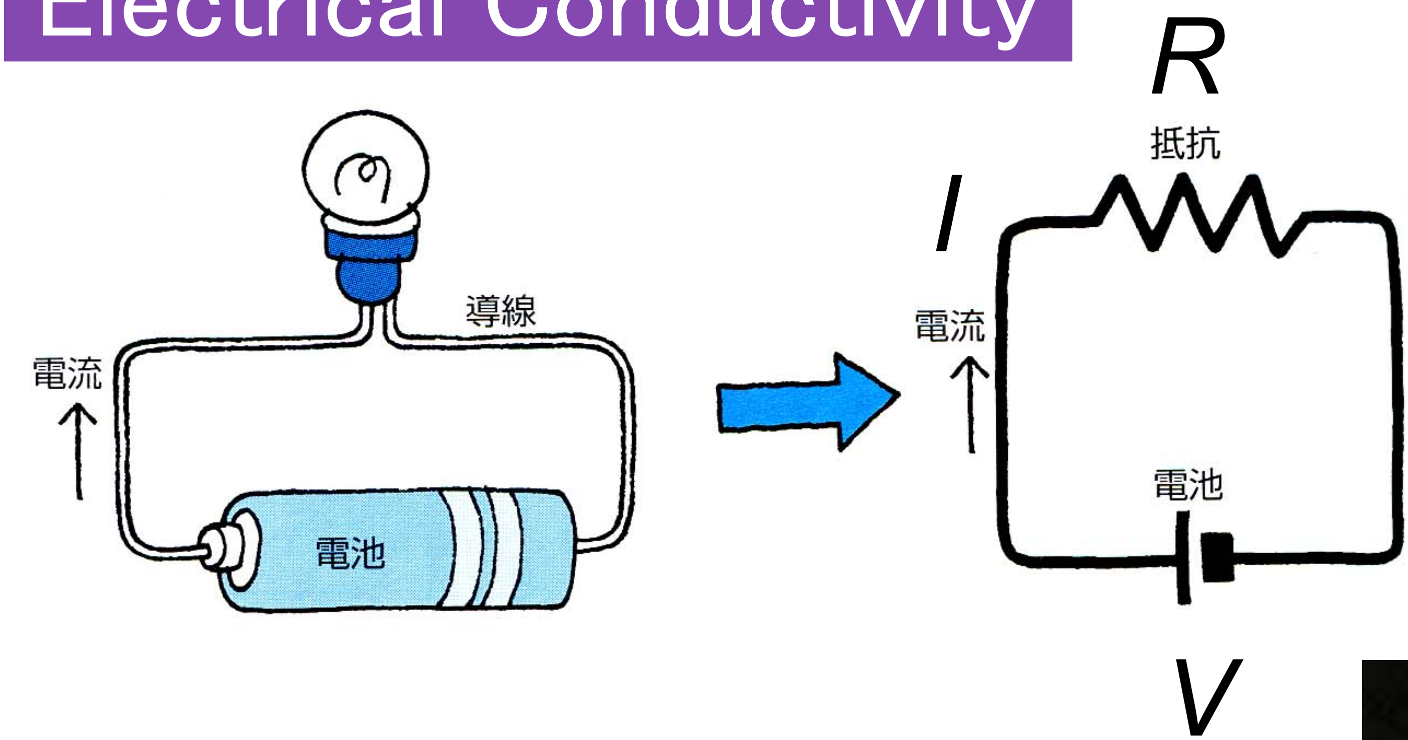
II. Frustration and Cu minerals

III. Rattling good materials

Outline

- Introduction to superconductivity
- Copper oxide superconductors: Preparation and Materials
- Mechanism of the superconductivity
- Future prospect

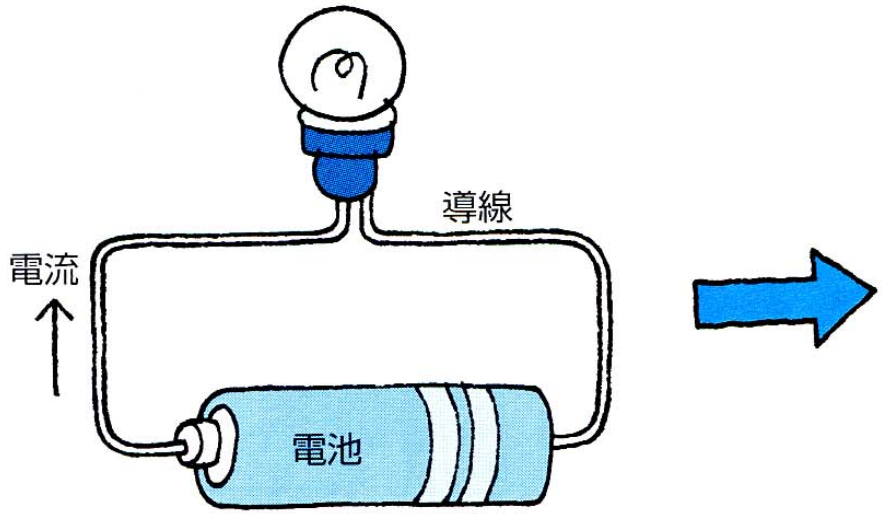
Electrical Conductivity

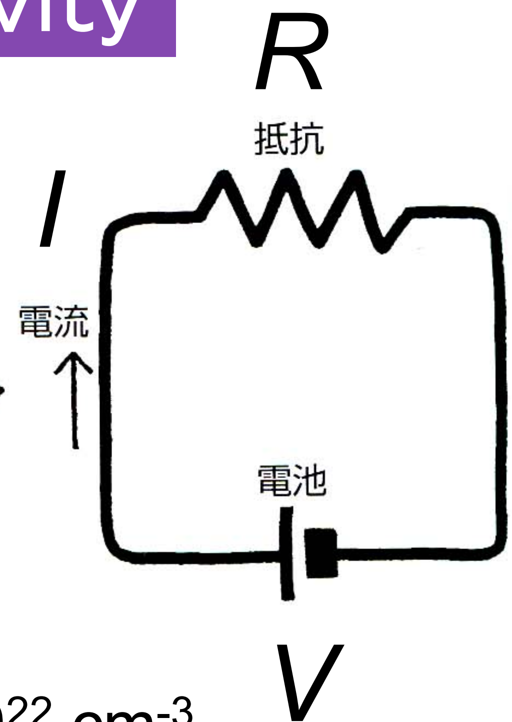


Ohm's law

$$\boxed{V = R \times I}$$

Electrical Conductivity

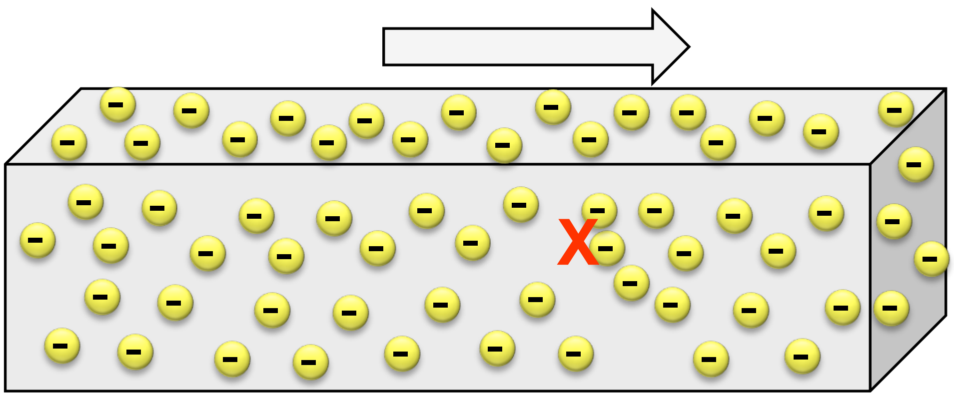




Ohm's law

$$V = R \times I$$

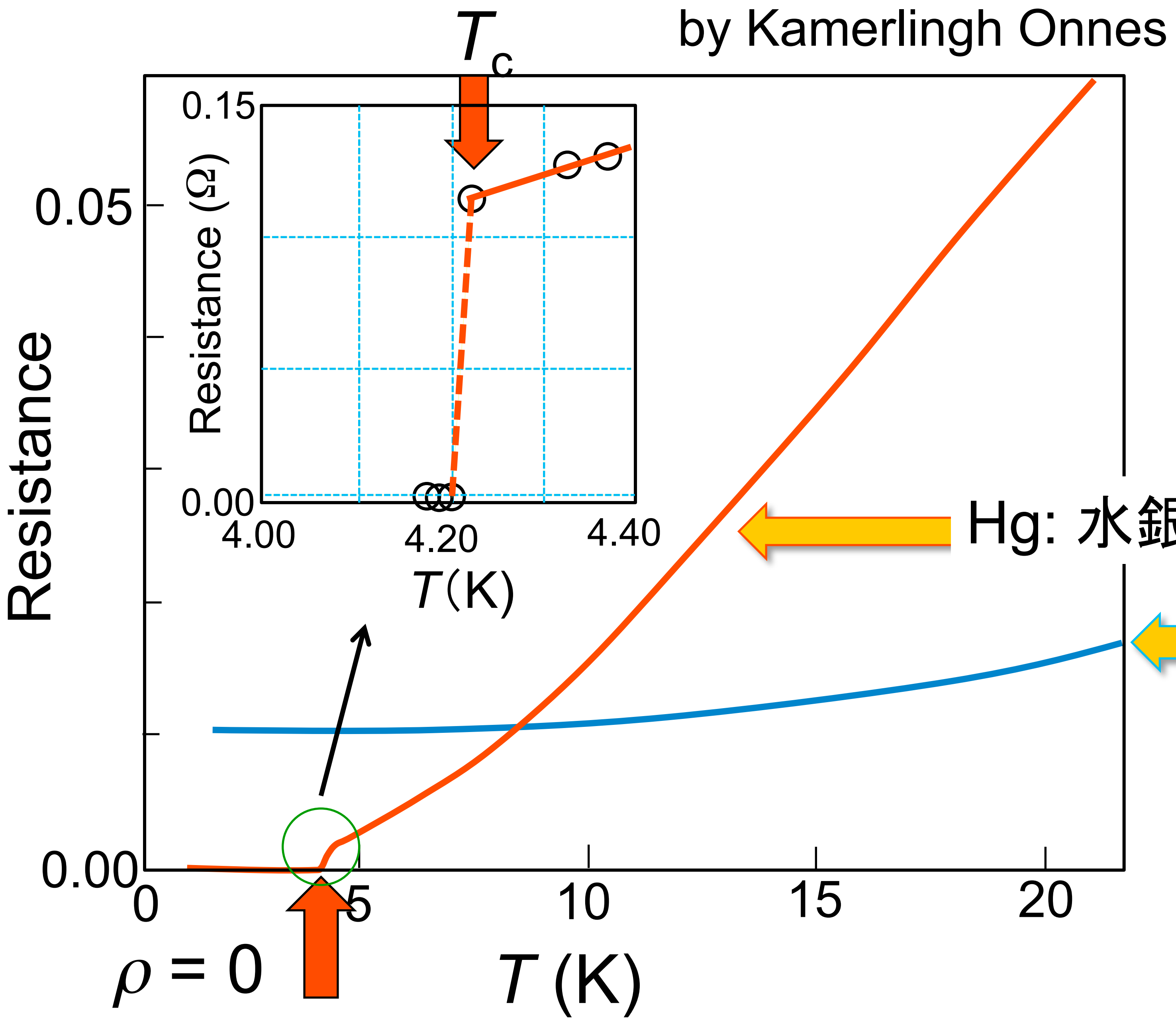
"free" electrons in a metal ～10^{22} cm^{-3}

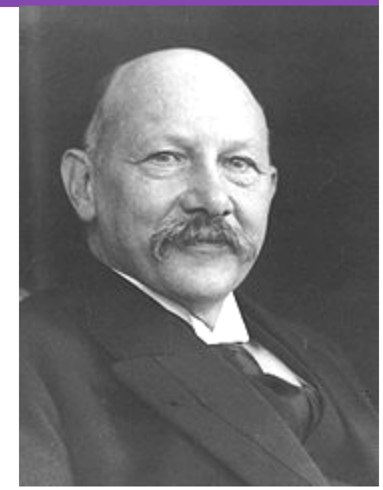


electron scattering → resistivity

Discovery of superconductivity in 1911

by Kamerlingh Onnes



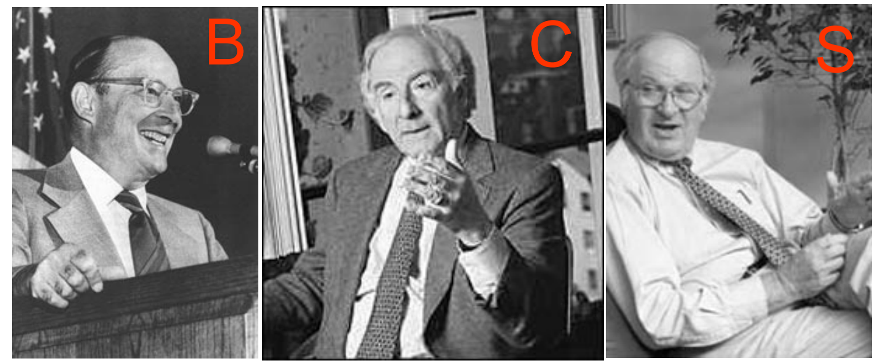


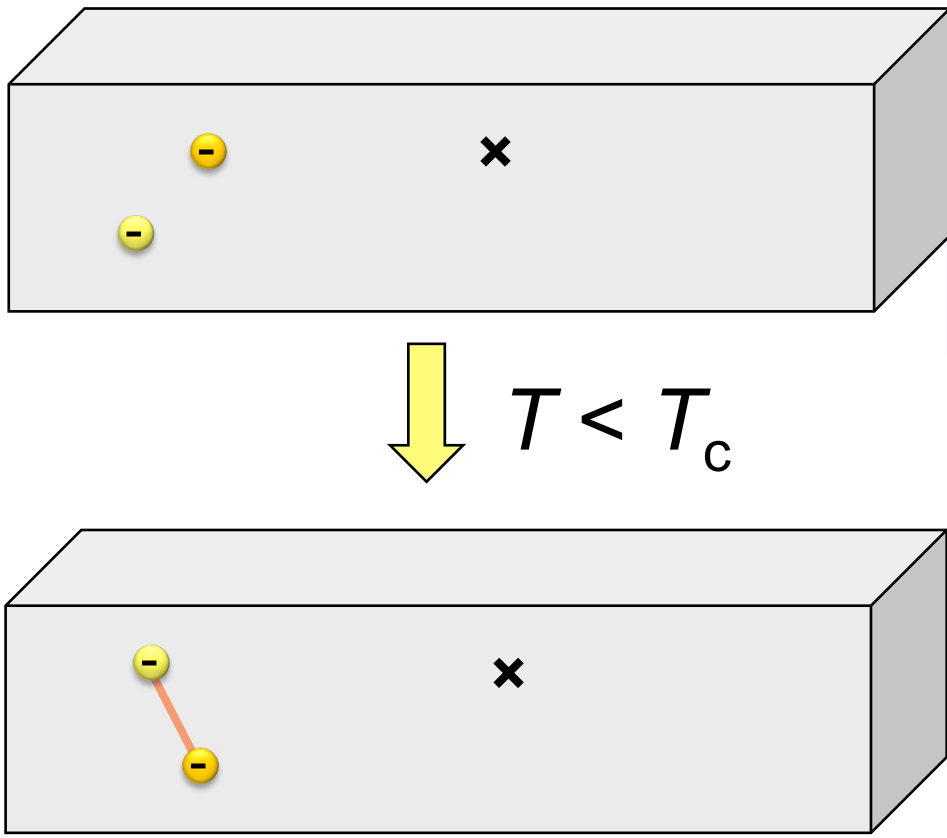
Nobel prize
1913

Why?

BCS theory: Bardeen-Cooper-Schrieffer

Nobel prize in 1972





$R \neq 0$

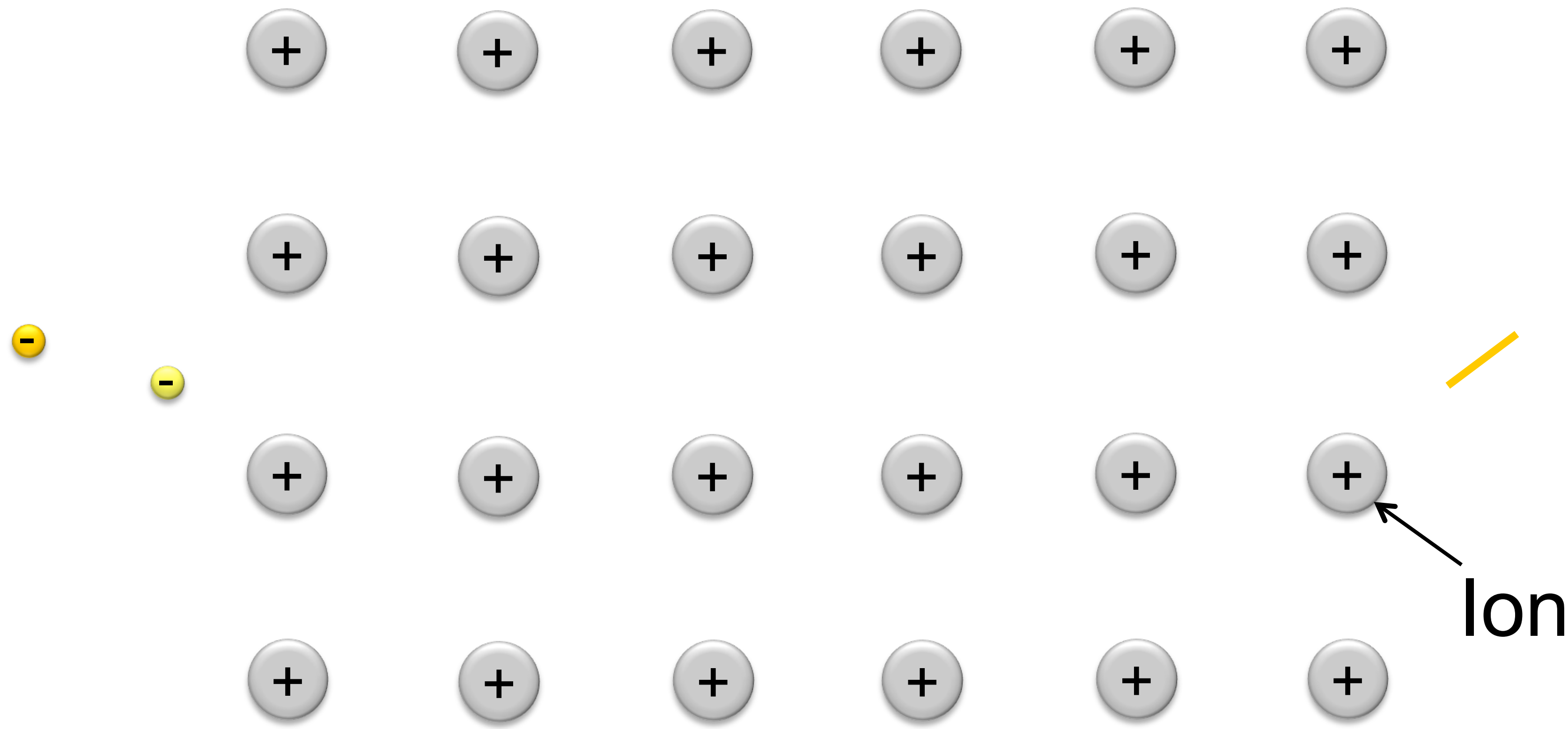
Two electrons form a pair
→ Cooper pair

$R = 0$

not scattered!

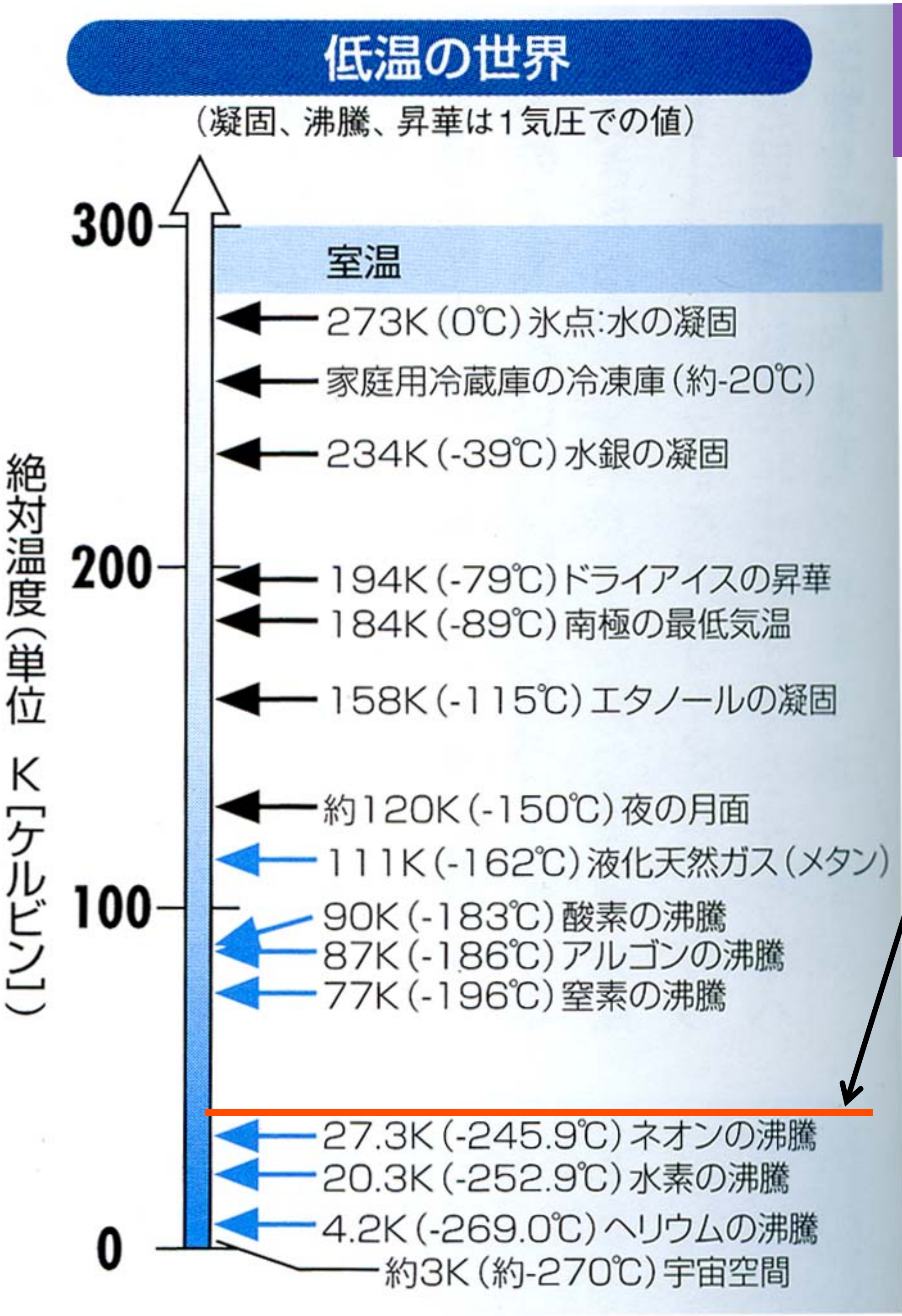
Mechanism of superconductivity

What makes a Cooper pair?



Vibrations of ions (phonons) generate the attractive interaction.
T_c ≈ vibration energy×0.1 ≈ 30 K

⇨ **BCS wall**



Temperature

室温:300 K

T_c is too low!

"BCS wall"

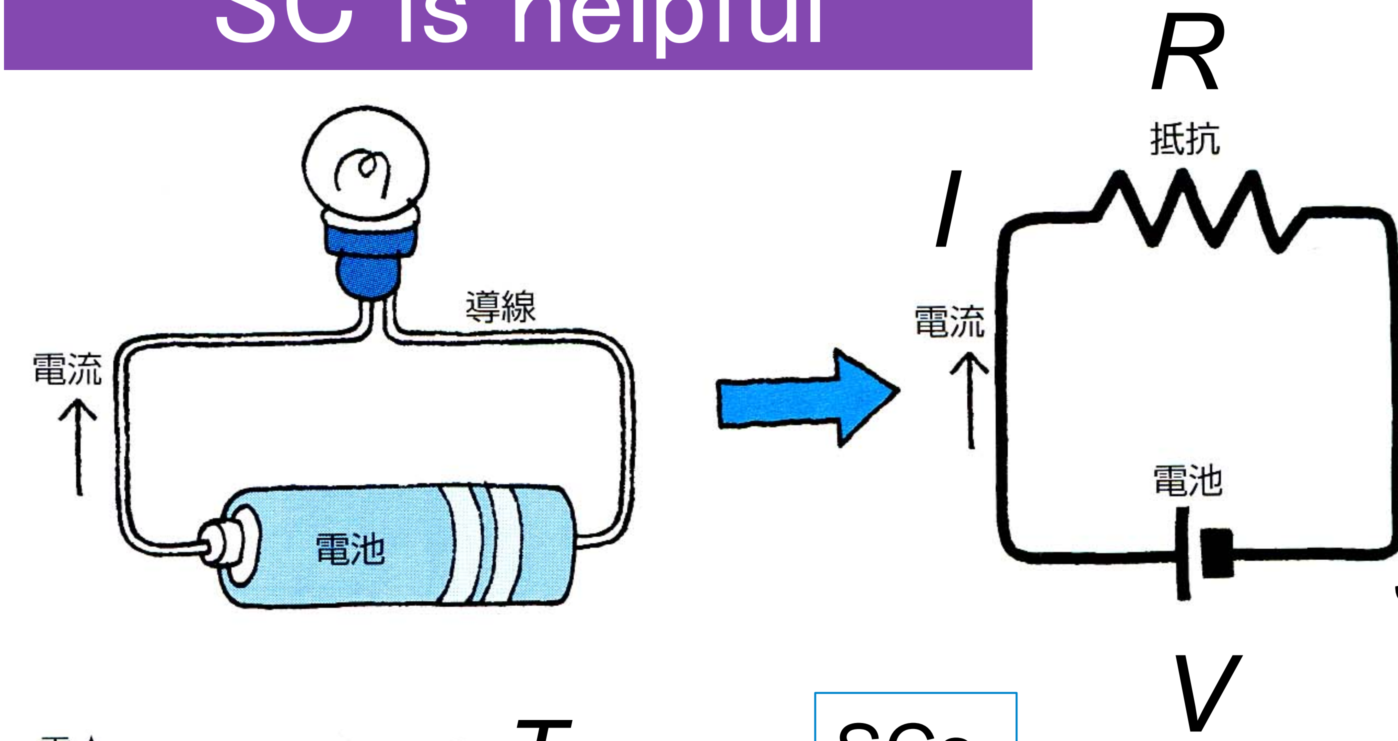
$T_c < 30$ K

Liquid Nitrogen: 77 K

Helium: 4.2 K

-273℃

SC is helpful

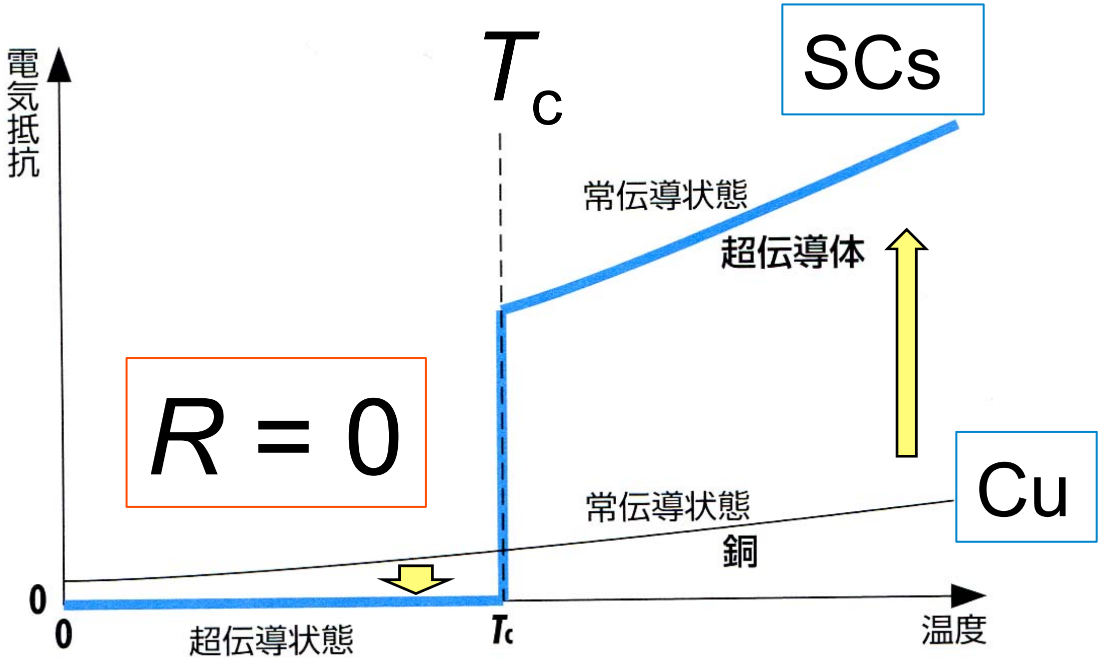


Ohm's law

$V = R \times I$

Joule heating

$R \times I \times I$

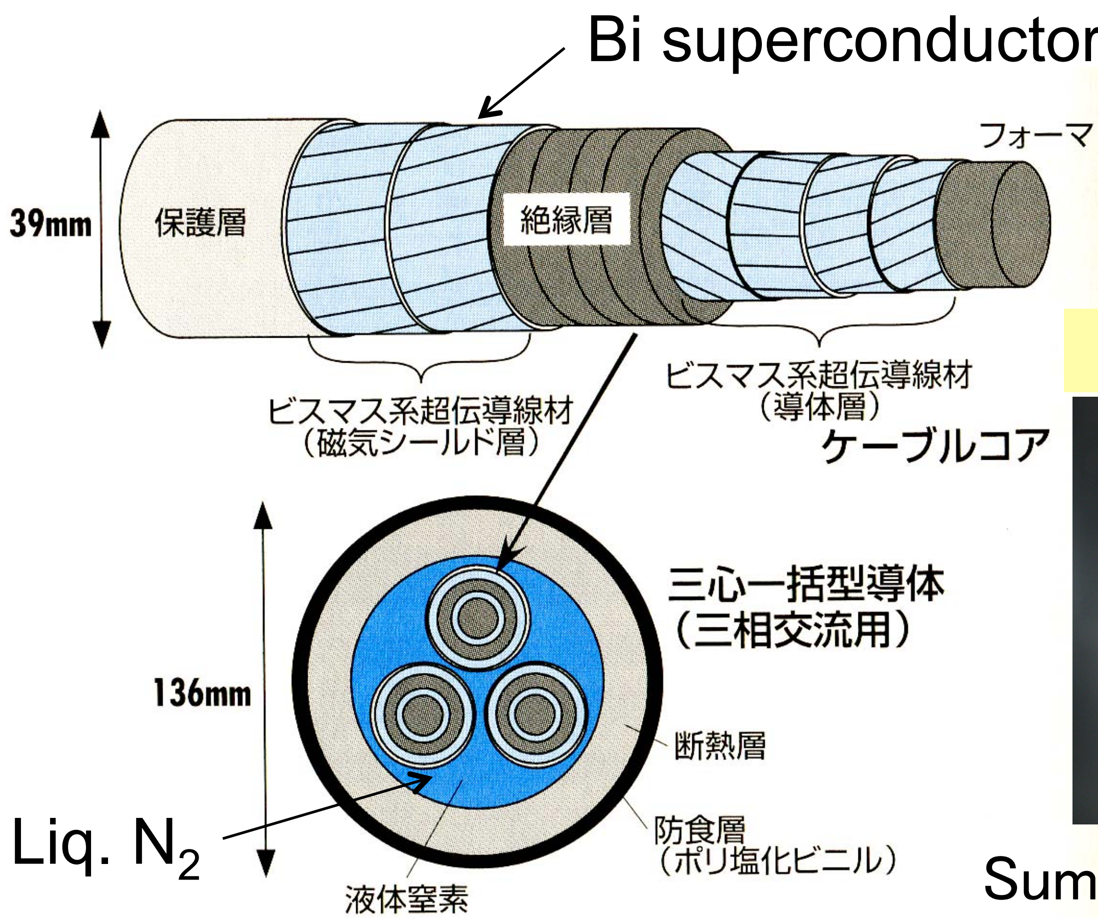


If $R = 0$,
no Joule heating,
no energy loss!

$R < 10^{-24}\ \Omega$

Superconducting cables

- 100 times larger current
- Limited space in an underground public utility conduit
- Total energy loss less than half even with liq N_2 cooling



Power Cable

Sumitomo Electric Industries, Ltd.

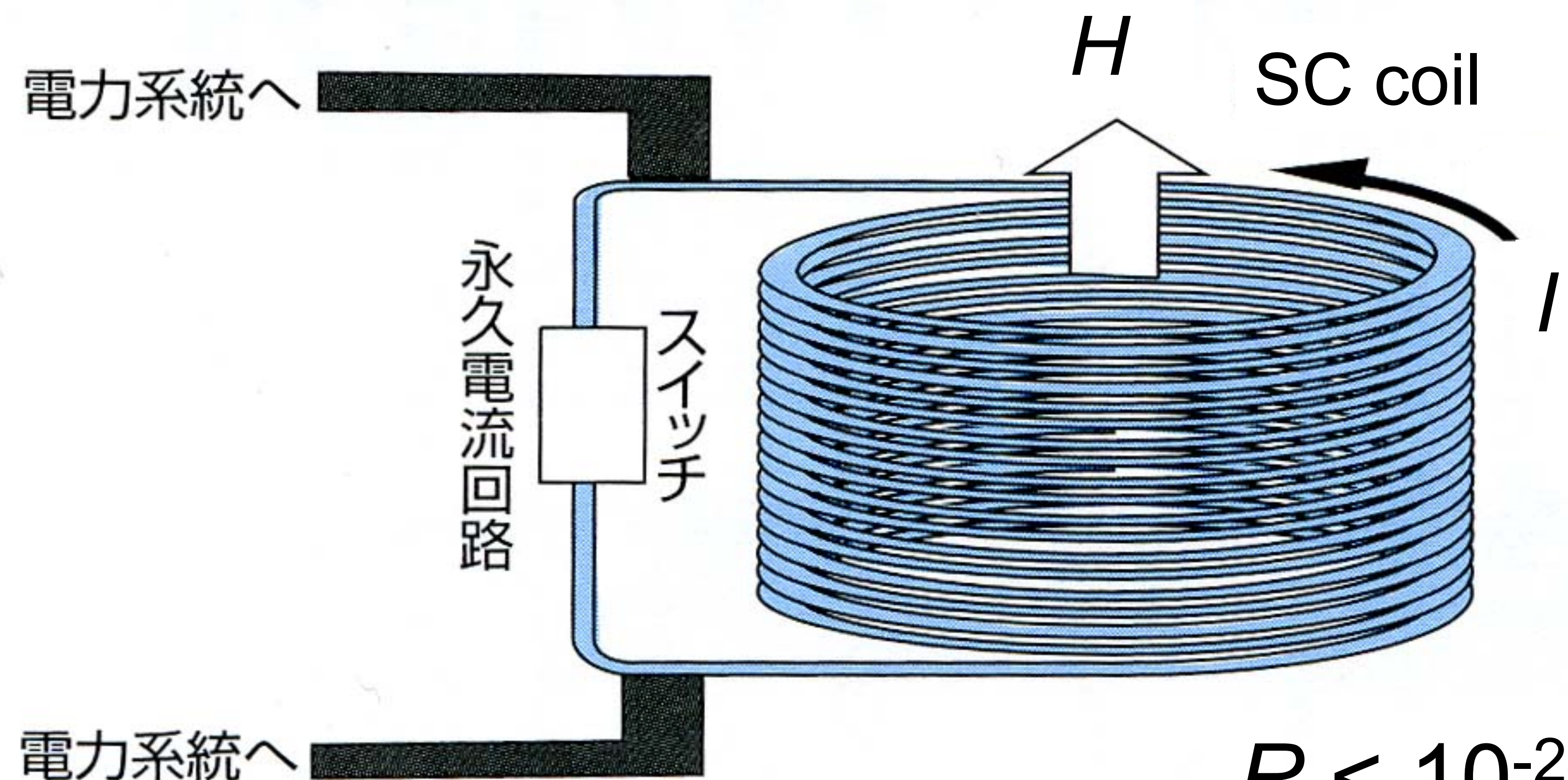
Global superconducting grid with natural energy generators

proposed by Koichi Kitazawa

Strong magnets

- Superconducting magnets
- Electric power storage

Persistent current



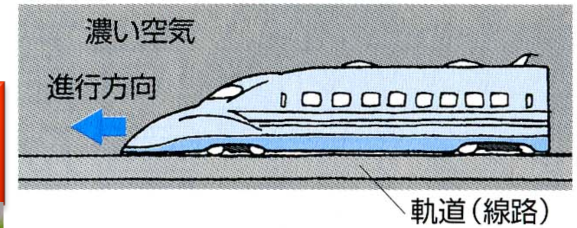
$R < 10^{-24}\ \Omega$

Magnetic levitated train

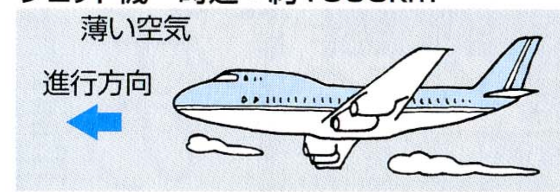
Max speed: 581 km/h

JR Central HP

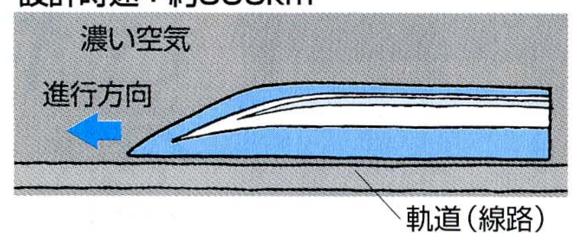
新幹線　時速：200〜300km



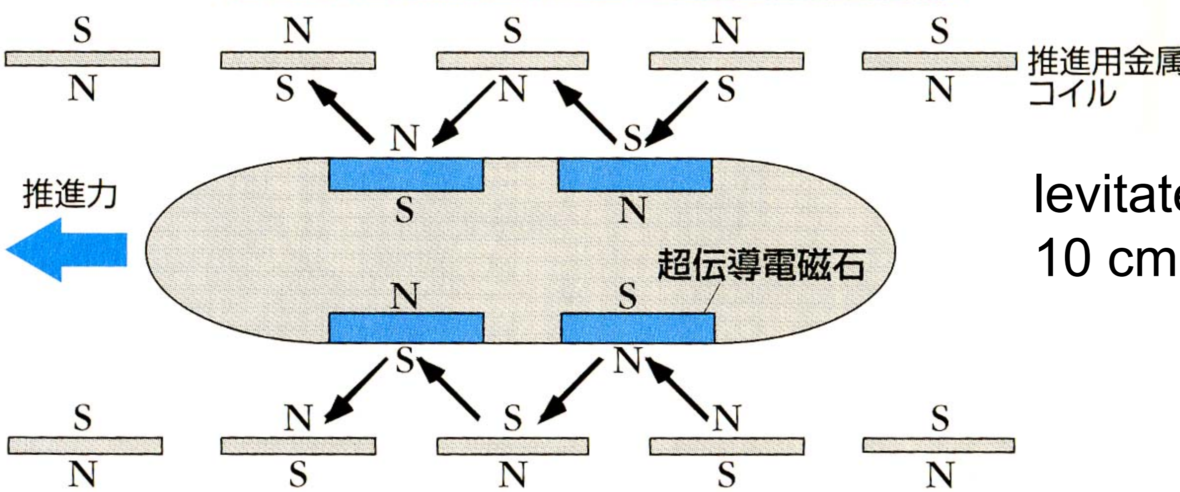
ジェット機　時速：約1000km



リニアモータカー
設計時速：約500km

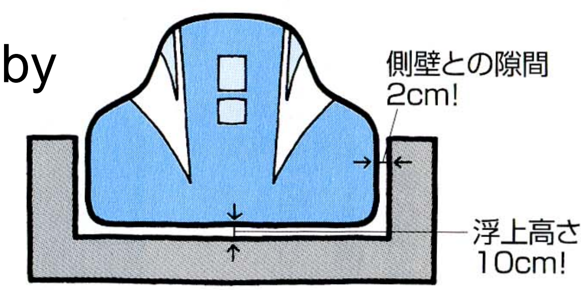


リニアモータカーが進む原理



levitated by 10 cm!

高速走行状態のリニアモータカー



超伝導方式は車両が高く浮上するので安全!

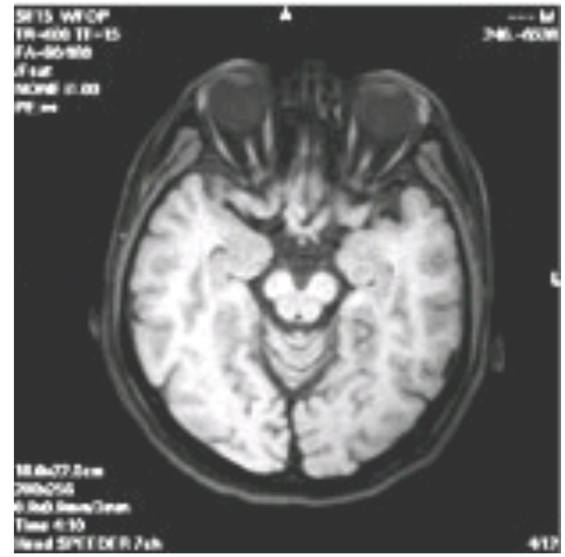
High–field applications

Ship motor

Consortium: 8 Entities

MRI

B = 3,000 ~ 15,000 gauss



Toshiba Medical HP

Outline

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- Copper oxide superconductors: Preparation and Materials
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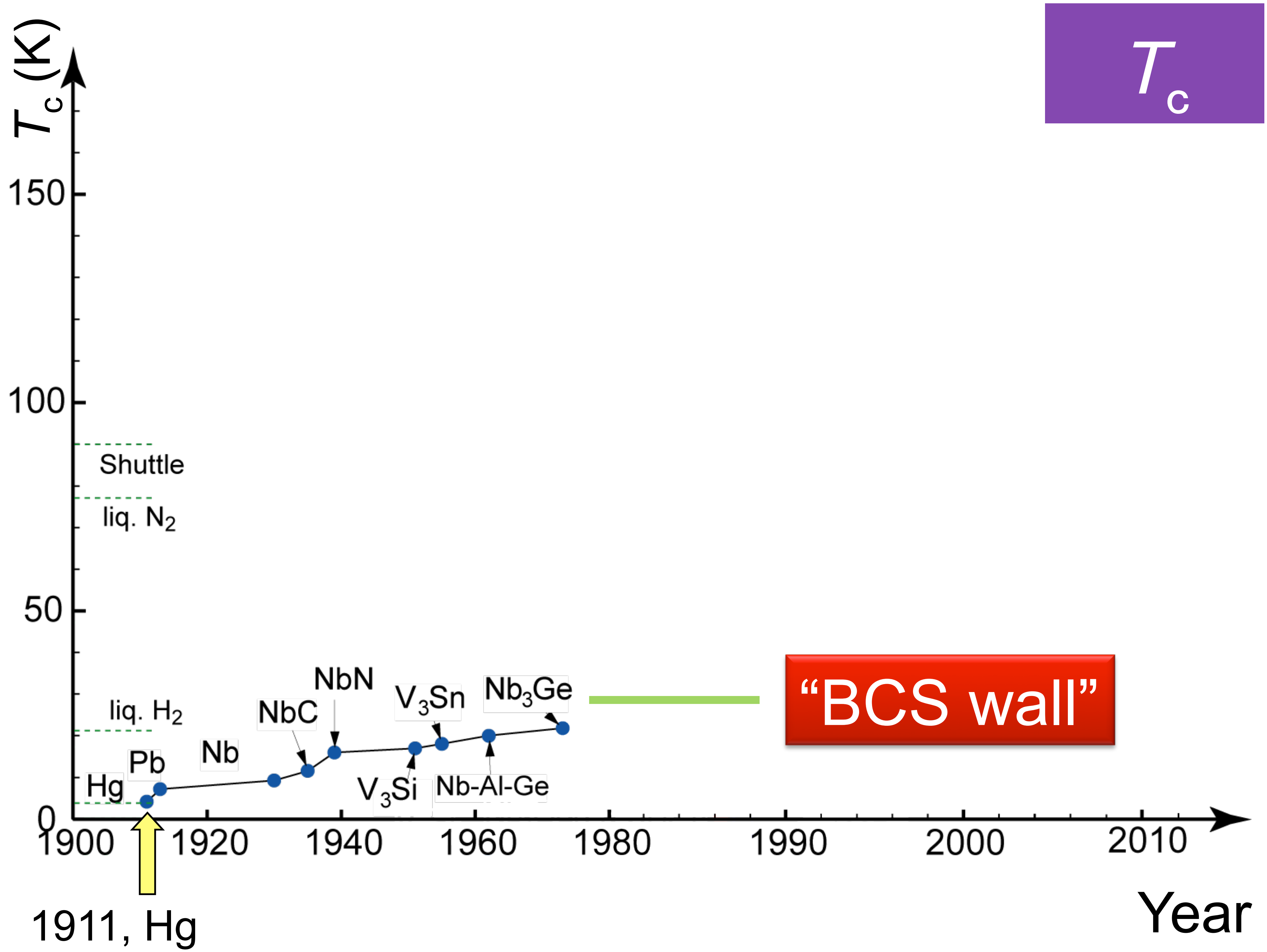
- Future prospect



T_c
T_c (K)
150
100
50
0
Shuttle
liq. N_2
liq. H_2
Hg
Pb
Nb
NbC
NbN
V_3Si
V_3Sn
Nb-Al-Ge
Nb_3Ge
"BCS wall"
1900
1920
1940
1960
1980
1990
2000
2010
Year
1911, Hg

J. G. Bednortz
&
K. A. Müller

Physics Novel Prize in 1987

Summer in 1987 at the Bando lab. in Kyoto Univ.

Discovery of a copper oxide superconductor

1986

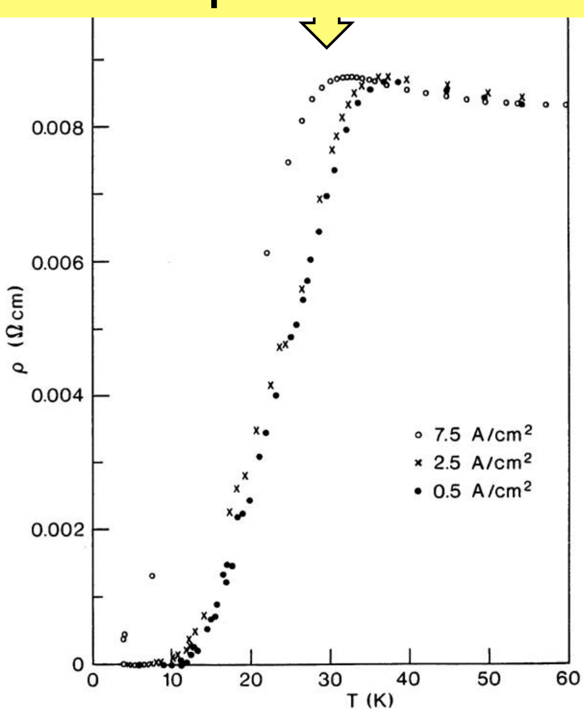
Z. Phys. B – Condensed Matter 64, 189–193 (1986)

Condensed Matter
Zeitschrift für Physik B

Possible High T_c Superconductivity in the Ba-La-Cu-O System

"At the extreme forefront of research in superconductivity is the empirical search for new materials".

composi-
ples with
of three
cooling,
garithmic
increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, bute possibly also from $2D$ superconducting fluctuations of double perovskite layers of one of the phases present.



I. Introduction

"At the extreme forefront of research in superconductivity is the empirical search for new materials" [1]. Transition-metal alloy compounds of A 15 (Nb_3Sn) and B 1 (NbN) structure have so far shown the highest superconducting transition temperatures. Among many A 15 compounds, careful optimization of Nb–Ge thin films near the stoichiometric composition of Nb_3Ge by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest T_c = 23.3 K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high T_c's [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li–Ti–O system with onsets as high as 13.7 K was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high T_c [5]. Other oxides like perovskites exhibit superconductivity despite their small carrier concentrations, n. In Nb-doped $SrTiO_3$, with $n = 2 \times 10^{20}$ cm^{-3}, the plasma edge is below the highest optical phonon, which is therefore unshielded [6]. This large electron-phonon coupling allows a T_c of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound $BaPb_{1-x}Bi_xO_3$ by Sleight et al., also a decade ago [8]. The highest T_c in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carriers $n = 2$–4×10^{21} cm^{-3} [9]. Flat electronic bands and a strong breathing mode with a phonon feature near 100 cm^{-1}, whose intensity is proportional to T_c, exist [10]. This last example indicates that within the BCS mechanism, one may find still higher T_c's in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A mechanism for polaron formation is the Jahn-Teller effect, as studied by Höck et al. [12]. Isolated Fe^{4+}, Ni^{3+} and Cu^{2+} in octahedral oxygen environment

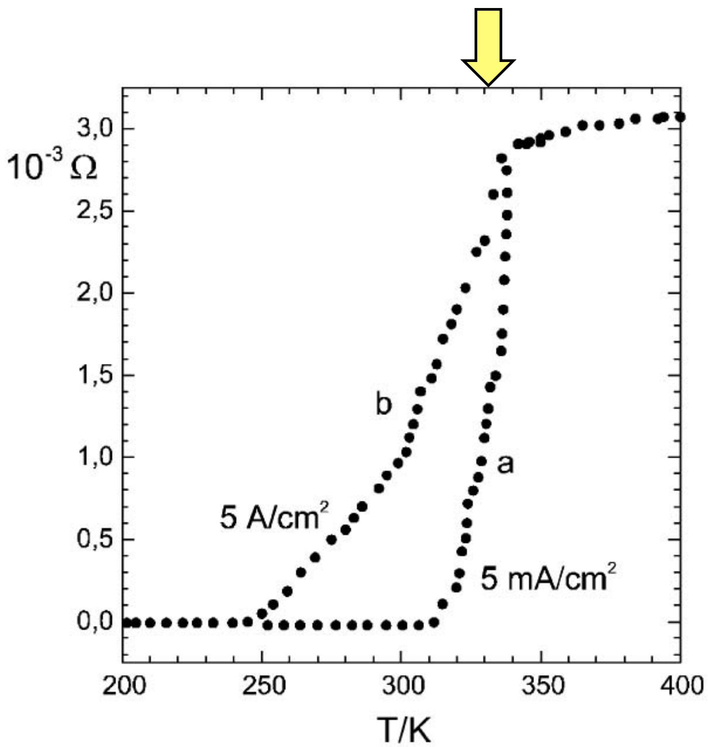
USO

"Uso" means "lie" in Japanese.

UFO = Unidentified Flying Object

USO = Unidentified Superconducting Object

T_c = 330 K!?



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Physica C 351 (2001) 78 81

PHYSICA C

www.elsevier.nl/locate/physc

$PbCO_3 \cdot 2PbO + Ag_2O$ and $PbCO_3 \cdot PbO + Ag_2O$ (PACO) systems: route for novel superconductors

D. Djurek [a,*], Z. Medunić [a], A. Tonejc [b], M. Paljević [c]

[a] *A. Volta Applied Ceramics (AVAC), Fundamental and Applied Research, Kesten brijeg 5, HR-10000 Zagreb, Croatia*

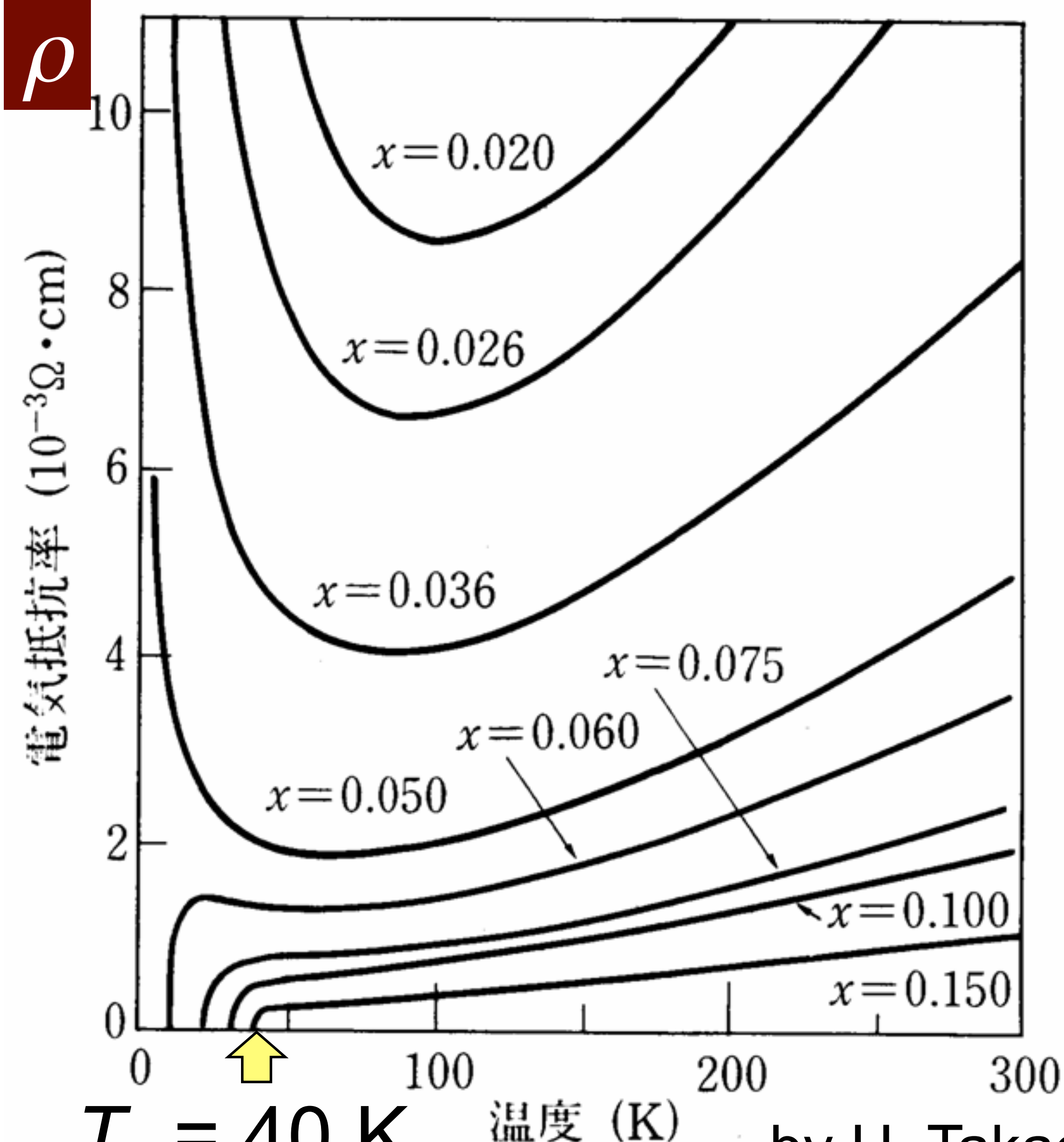
[b] *Department of Physics, Faculty of Sciences, Bijenička 32, HR-10000 Zagreb, Croatia*

[c] *Ruđer Bošković Institute, Bijenička 54, HR-10000 Zagreb, Croatia*

$La_{2-x}Sr_xCuO_4$

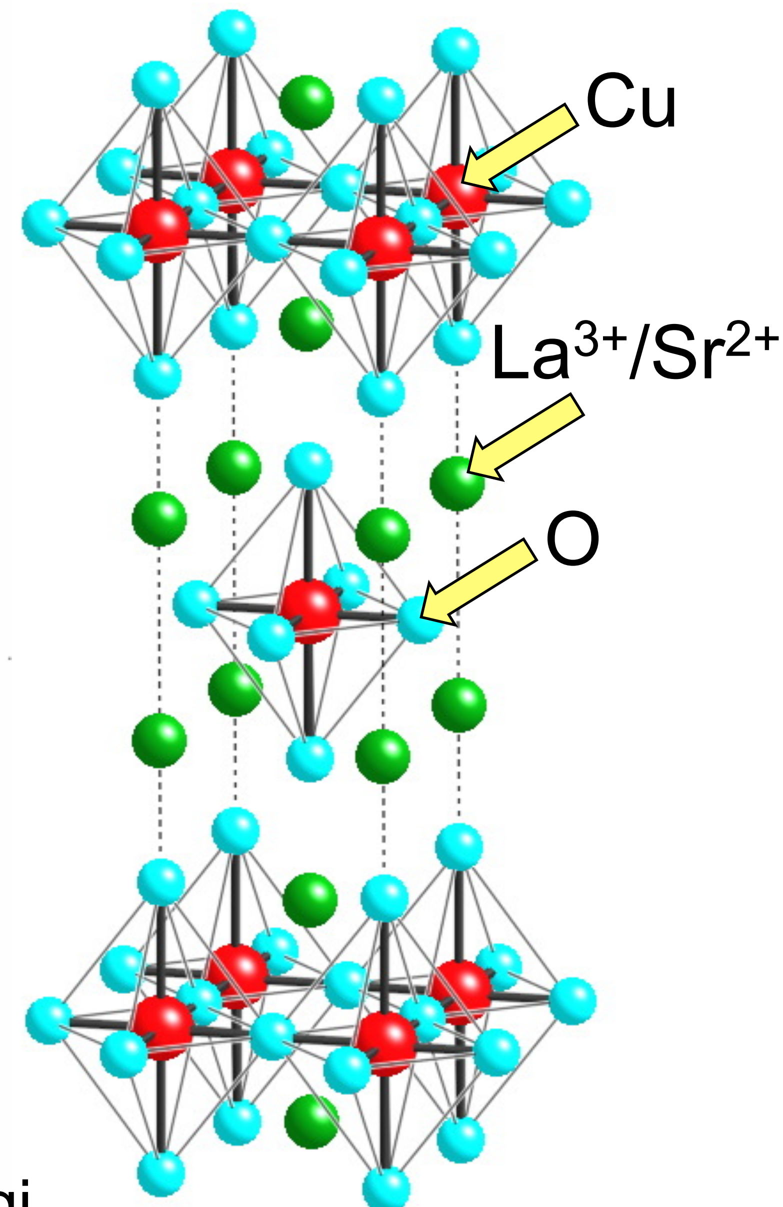
$Cu^{2+} \rightarrow Cu^{2+p}$ (hope doping), as La^{3+} is replaced by Sr^{2+}.

ρ

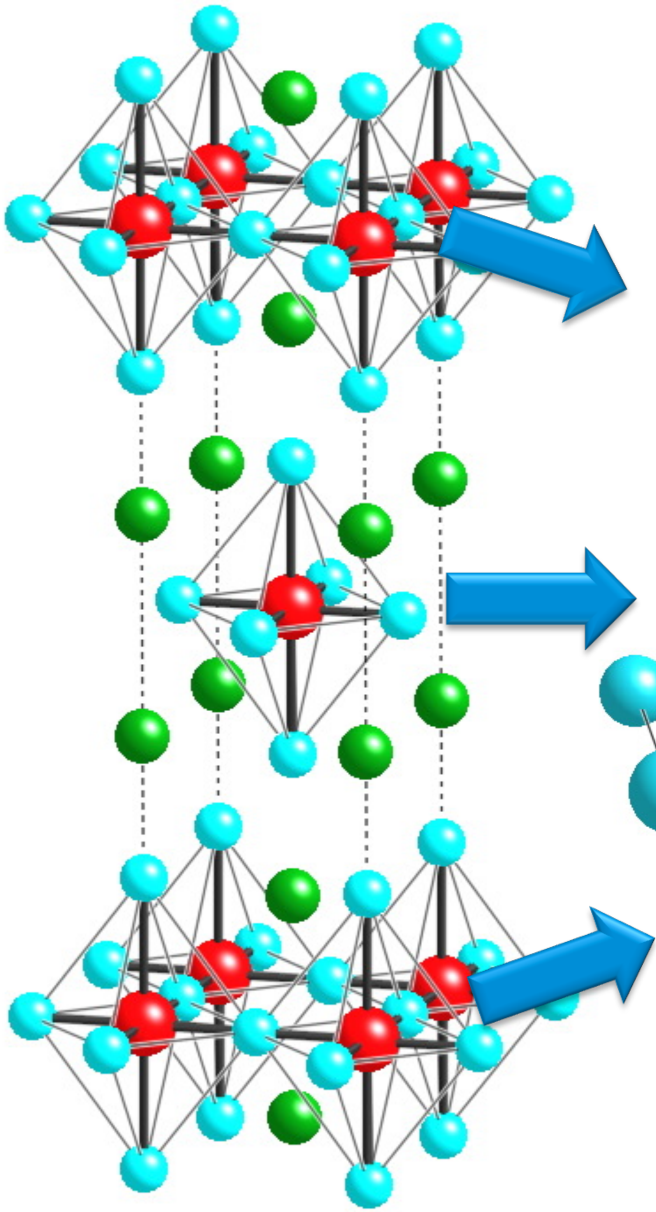


T_c = 40 K

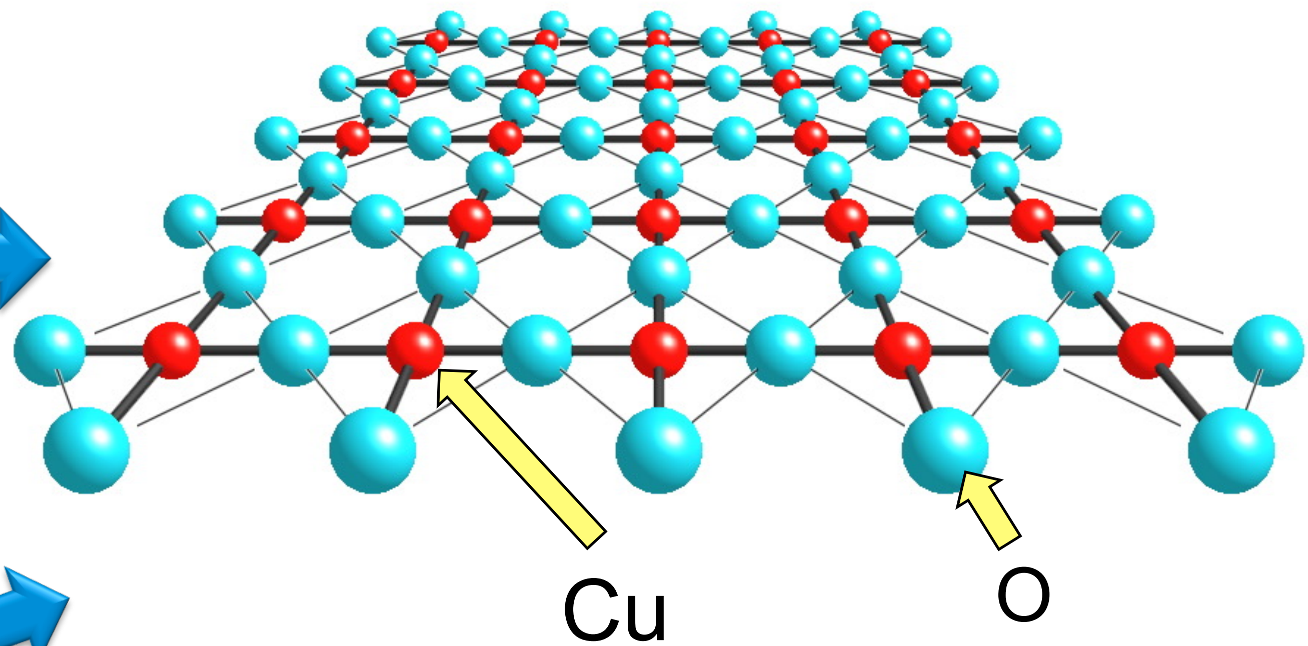
by H. Takagi



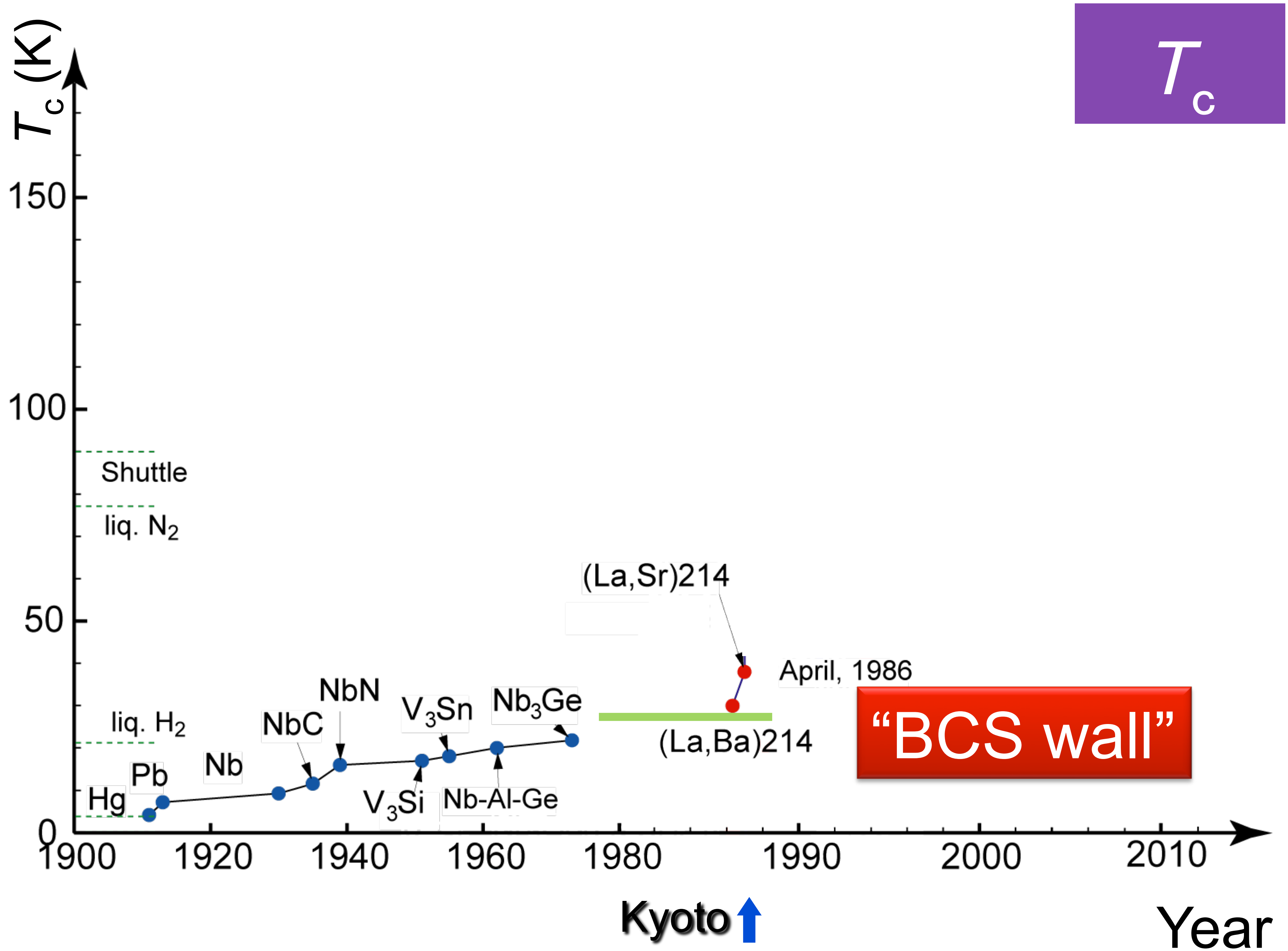
Playground for HTSC : CuO_2 Plane



Cooper pairs are formed in the CuO_2 plane,



when holes are introduced.



T_c
T_c (K)
150
100
50
0
Shuttle
liq. N_2
liq. H_2
Hg
Pb
Nb
NbC
NbN
V_3Si
V_3Sn
Nb-Al-Ge
Nb_3Ge
(La,Sr)214
April, 1986
(La,Ba)214
"BCS wall"
1900
1920
1940
1960
1980
1990
2000
2010
Kyoto
Year

Superconducting race

Periodic Table

Cu

	IA	IIA	IIIA	IVA	VA	VIA	VIIA		VIII		IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
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	57-71	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
7	87 Fr	88 Ra	89-103															

57-71	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
89-103	89 Ac	90 Th	91 Pa	92 U											

La-Ba-Cu-O
La-Sr-Cu-O

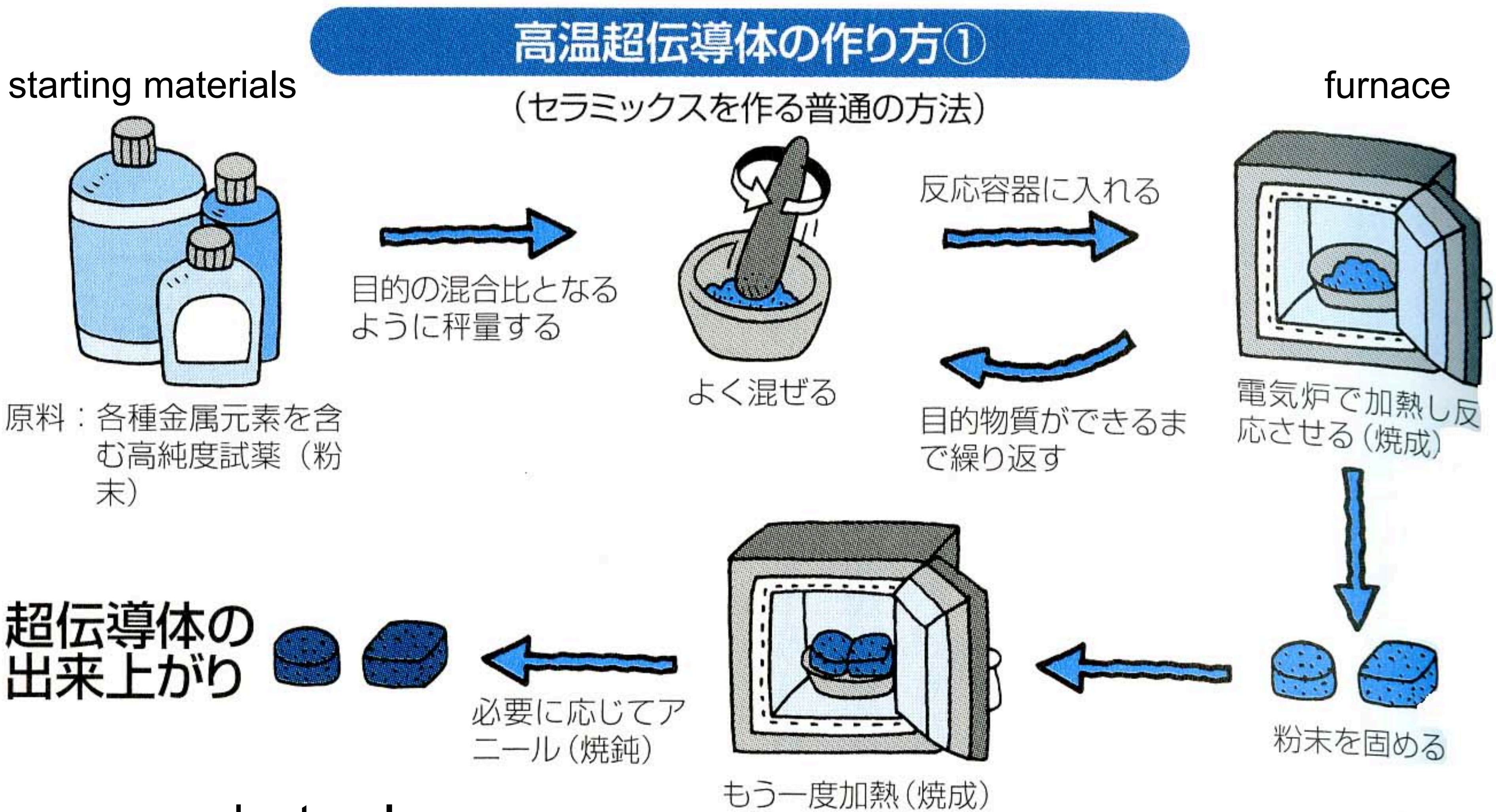
Let’s replace La by other Rare earth.

try to catch lightning in a bottle twice
= try to catch weather fish twice under willow (in Japanese).

How to make HTSCs

starting materials

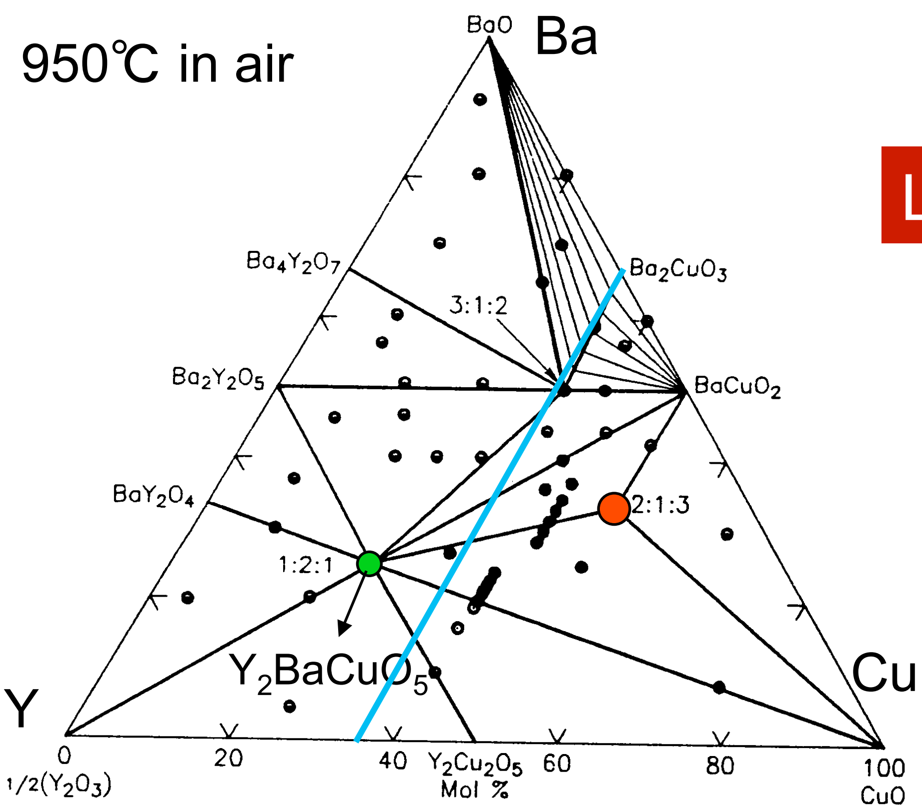
furnace



superconductors!

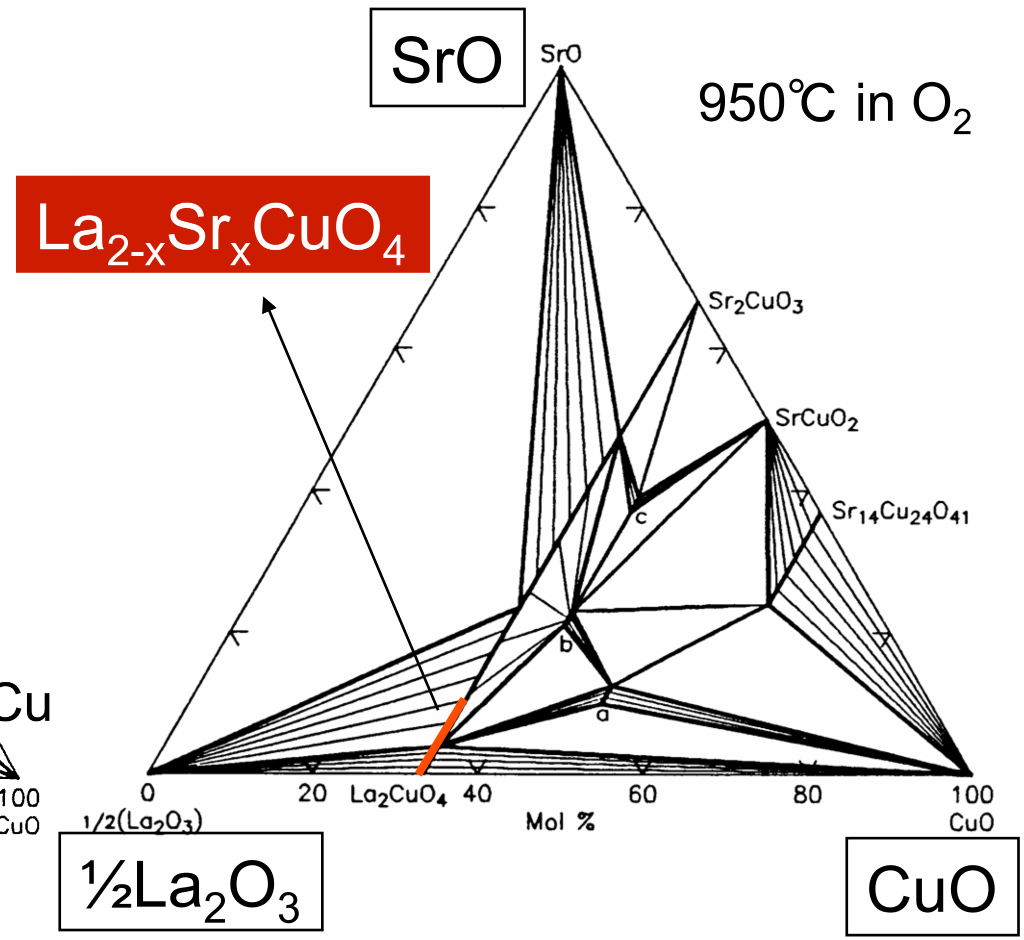
Phase Diagram: map for complex compounds

Y-Ba-Cu-O system



S.J. Hwe, et al., J. Am. Ceram. Soc. 70, C165 (1987)

La-Sr-Cu-O system

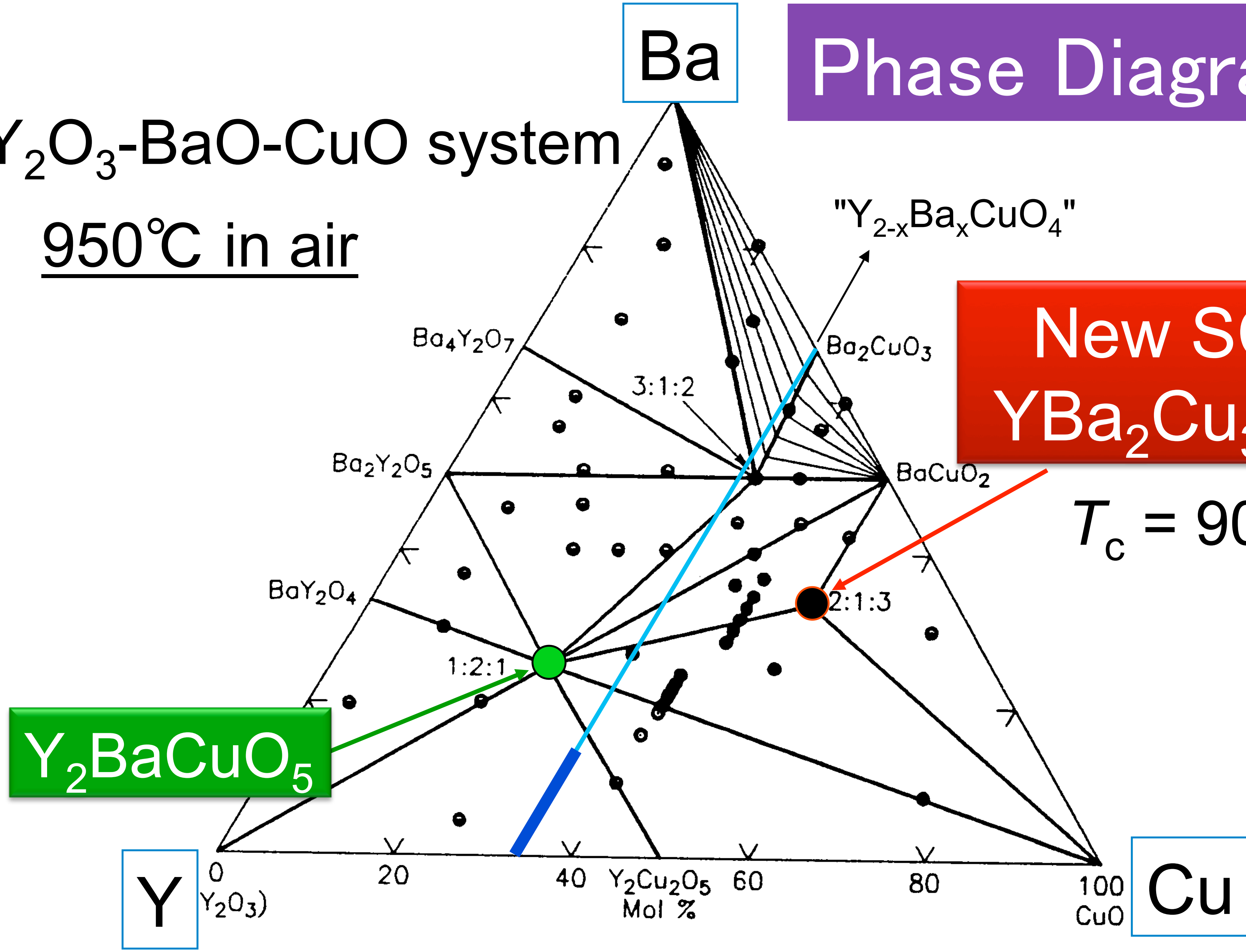


D.M. FeLeeuw, et al., J. Solid State Chem. 80, 276 (1989)

Phase Diagram

Y_2O_3-BaO-CuO system

950℃ in air



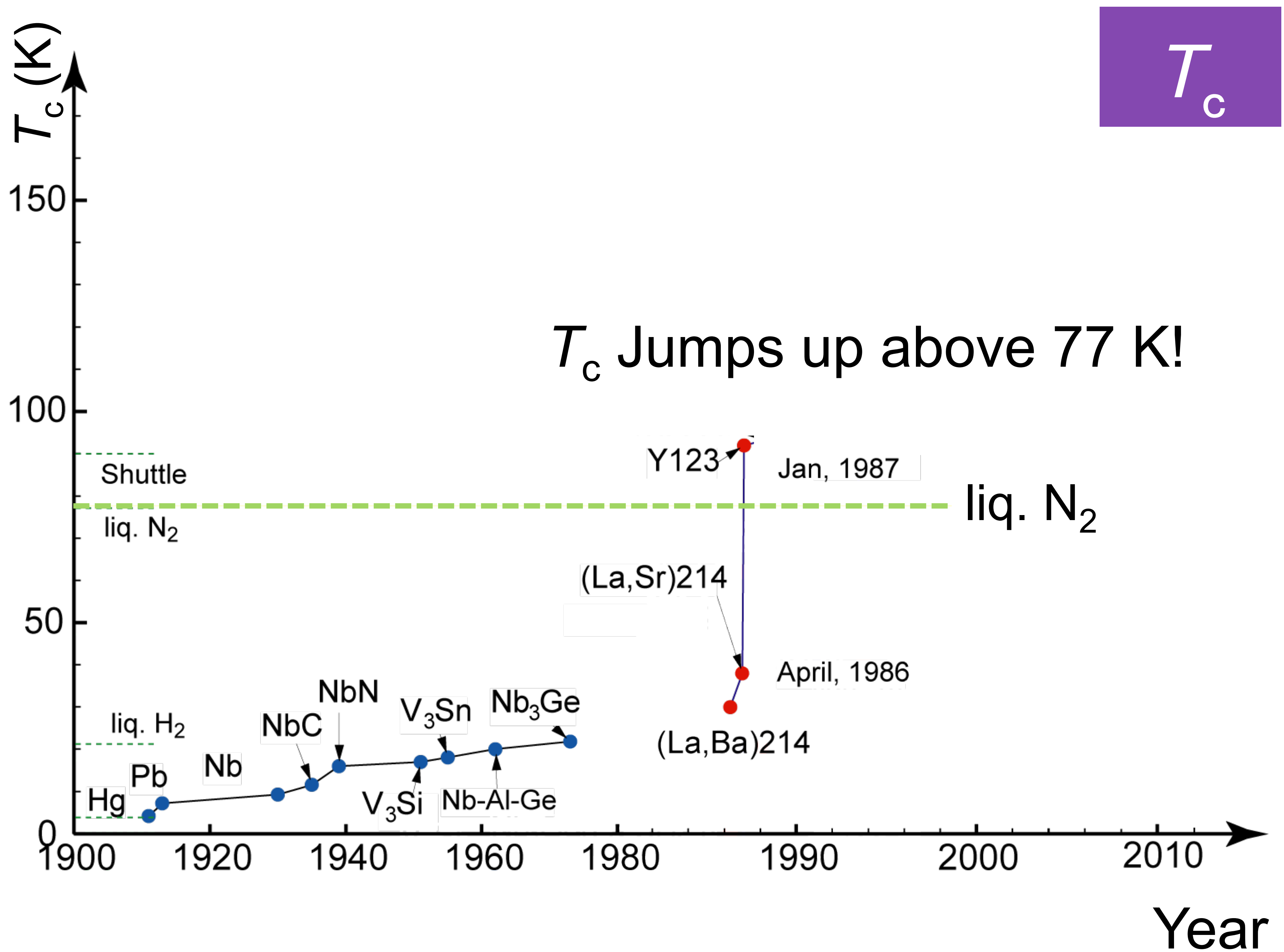
S.J. Hwe *et al.*, J. Am. Ceram. Soc. 70, C165 (1987)

Superconducting fever

Professor Koichi Kitazawa

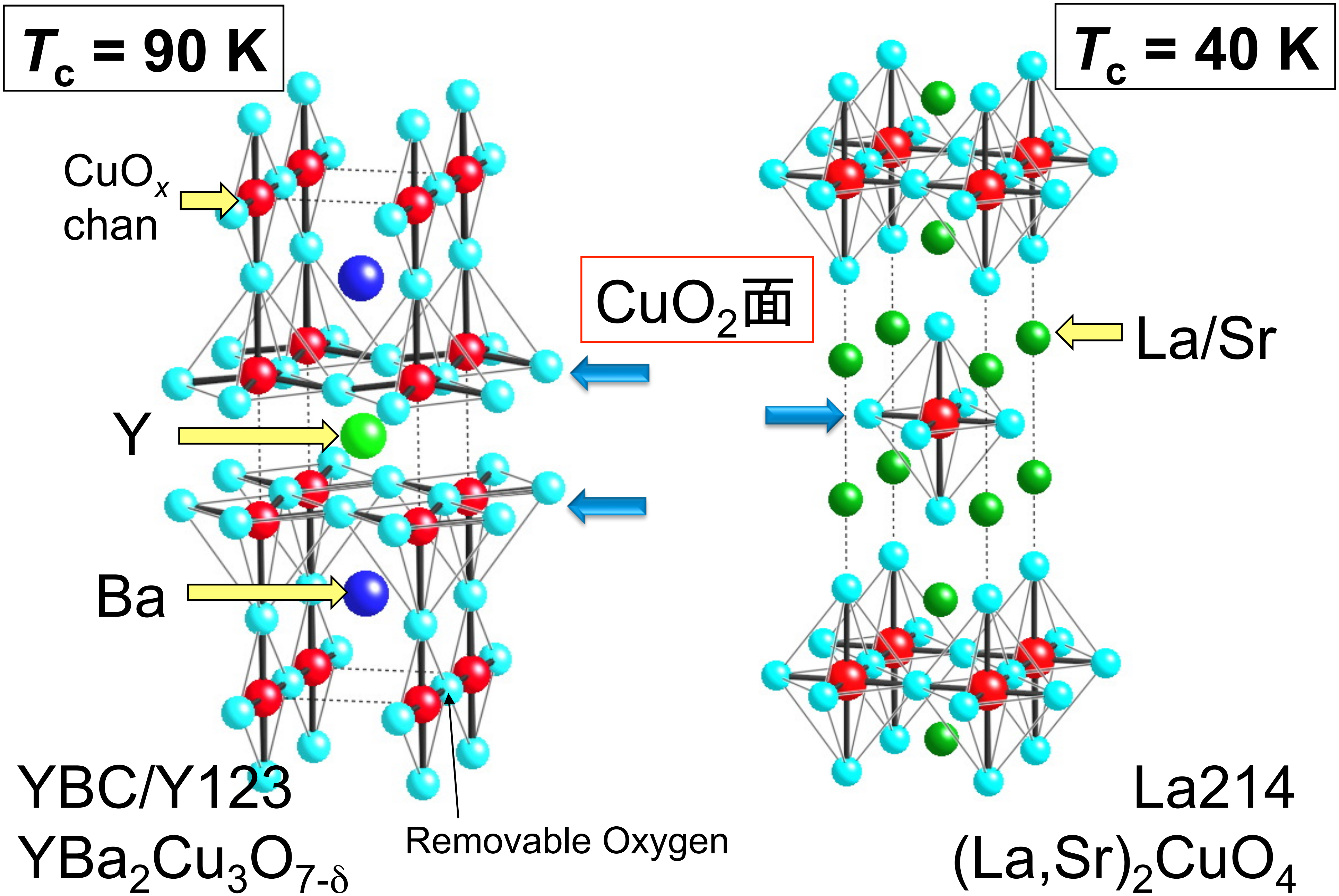
'Superconductivity Course'
by Shoutaro Ishinomori
Kodansha, 1988

8,400 yen @amazon.com

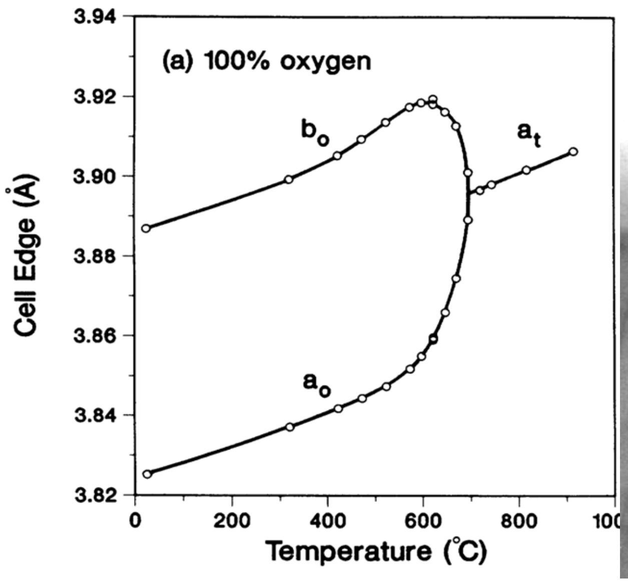


T_c
T_c (K)
150
100
50
0
Shuttle
liq. N_2
liq. H_2
Hg
Pb
Nb
NbC
NbN
V_3Si
V_3Sn
Nb-Al-Ge
Nb_3Ge
(La,Ba)214
(La,Sr)214
April, 1986
Y123
Jan, 1987
liq. N_2
T_c Jumps up above 77 K!
1900
1920
1940
1960
1980
1990
2000
2010
Year

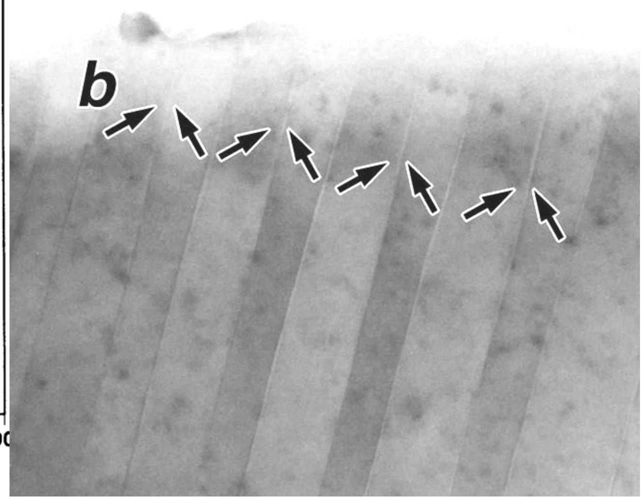
90 K Superconductor

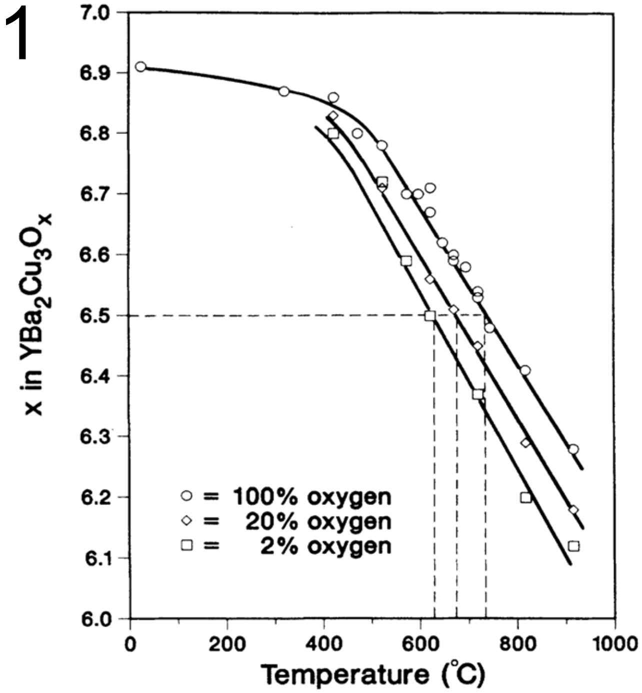


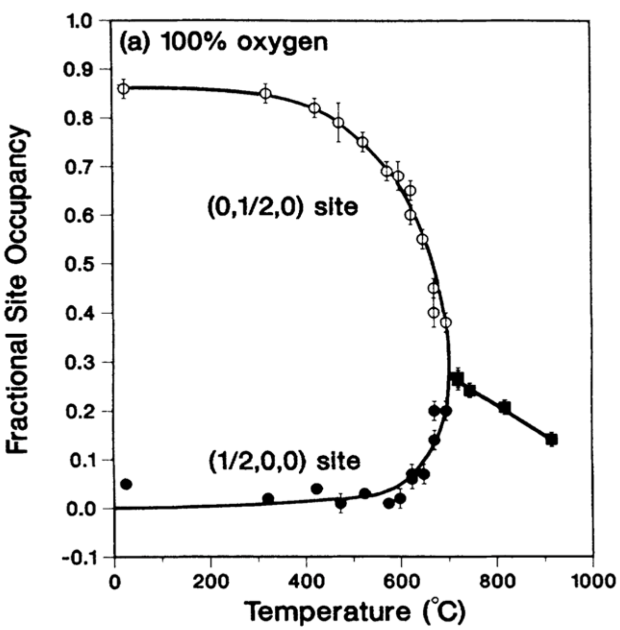
Interesting crystal chemistry in $YBa_2Cu_3O_{7-d}$

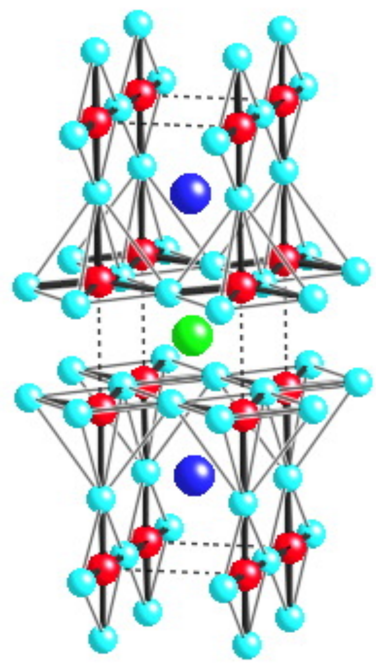


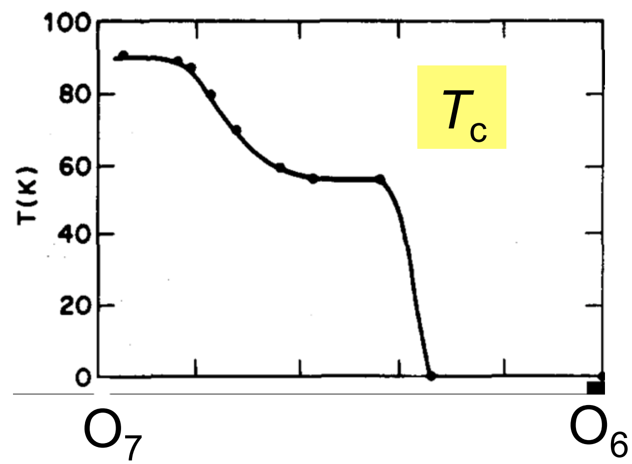
$0 \leq \delta \leq 1$







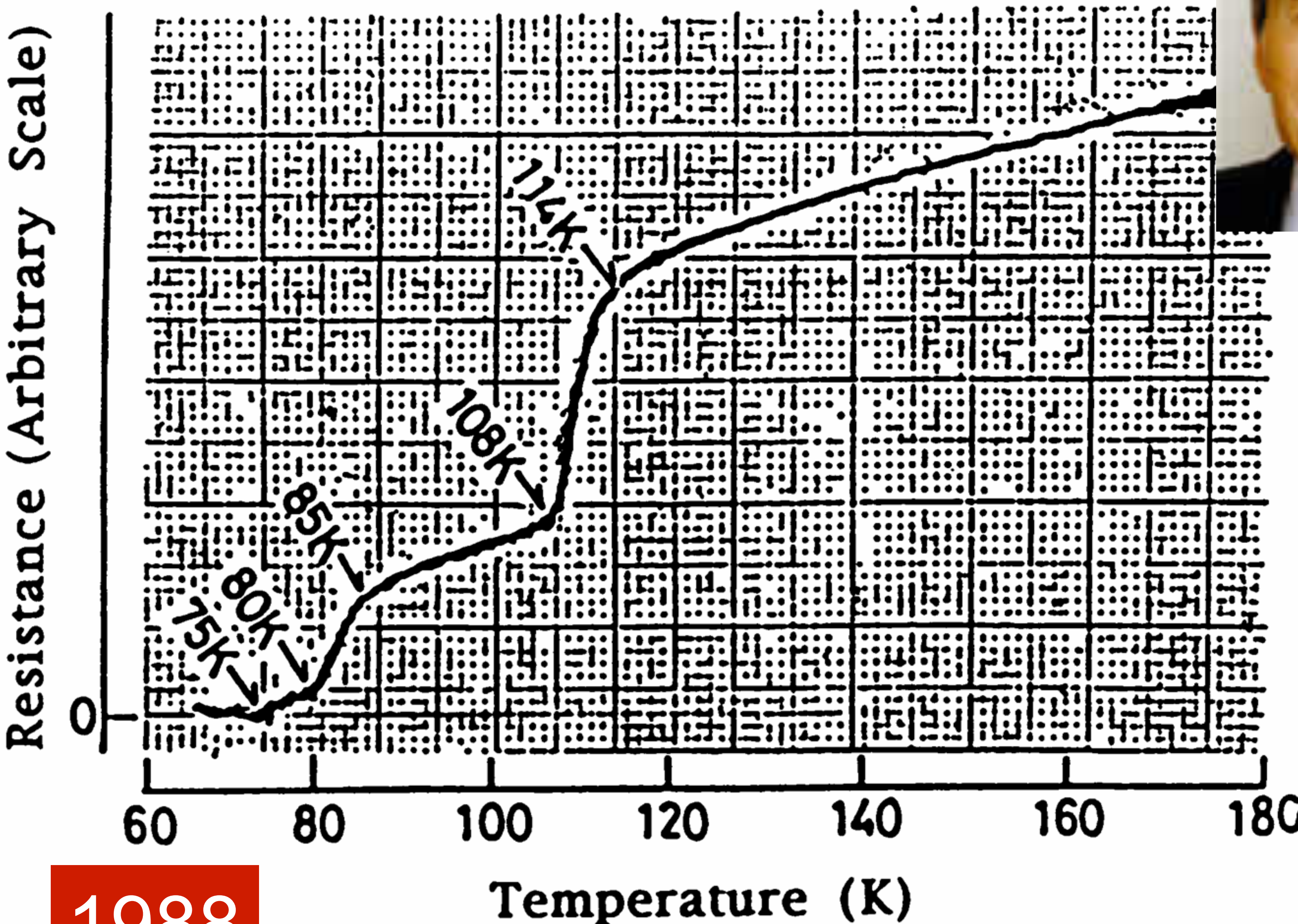




J.D. Jorgensen, *et al.*, Phys. Rev. B 36, 3608 (1987)

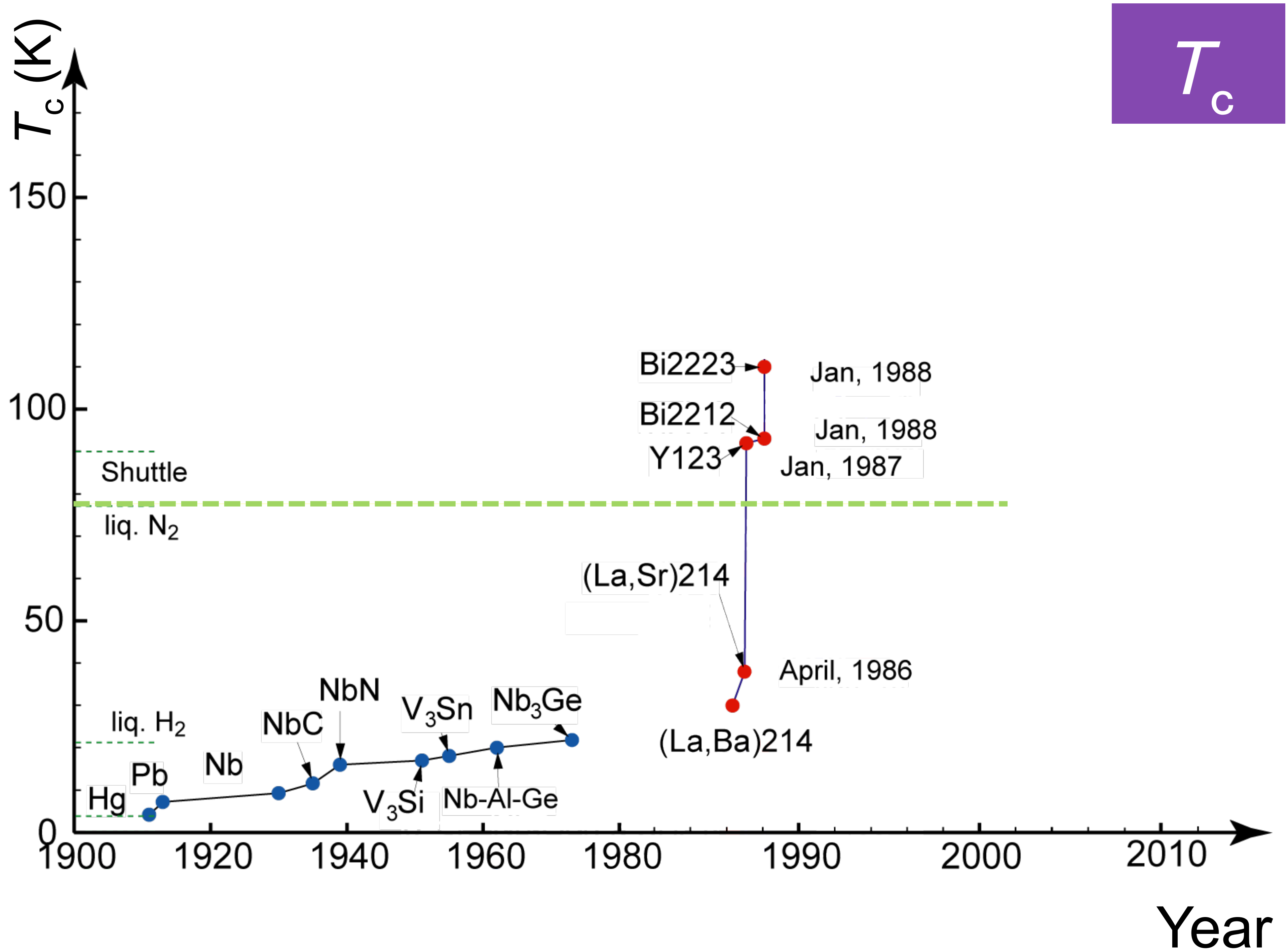
R.J. Cava, et al., Physics C 165, 419 (1990)

Hiroshi Maeda



1988

National Lab. at Tsukuba

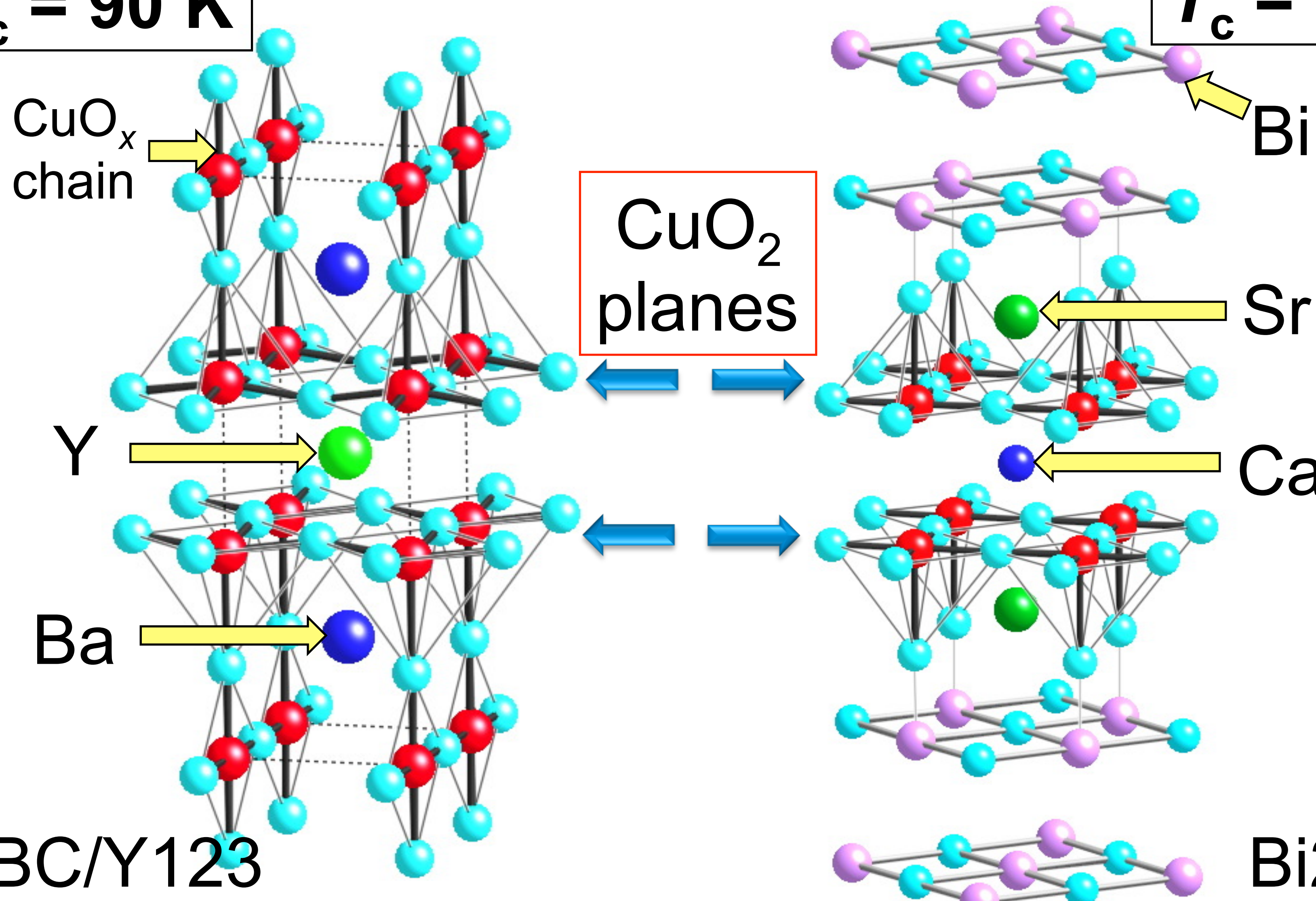


Tc
Tc(K)
150
100
50
0
1900
1920
1940
1960
1980
1990
2000
2010
Year
Shuttle
liq. N2
liq. H2
Hg
Pb
Nb
NbC
NbN
V3Si
V3Sn
Nb-Al-Ge
Nb3Ge
(La,Ba)214
(La,Sr)214
April, 1986
Y123
Jan, 1987
Bi2212
Jan, 1988
Bi2223
Jan, 1988

90 K Superconductors

T_c = 90 K

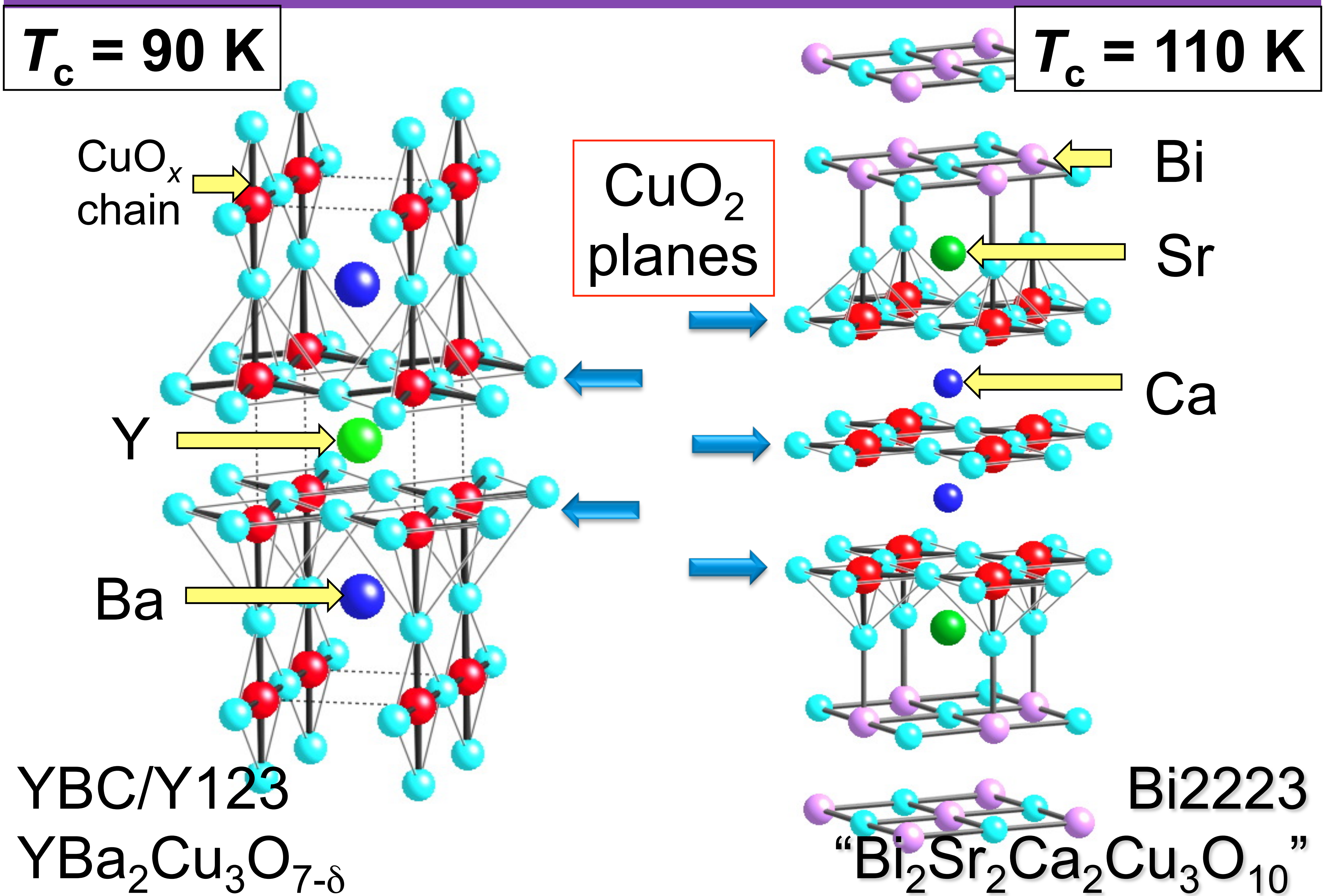
T_c = 90 K



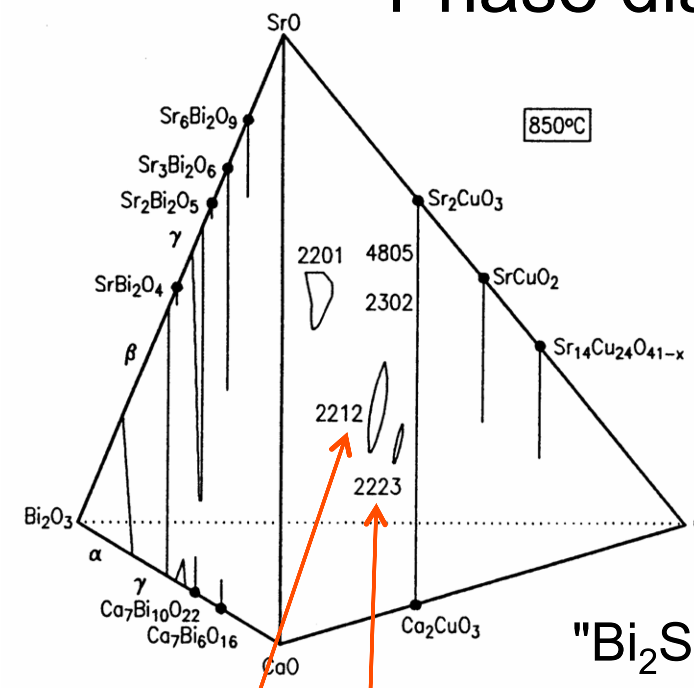
YBC/Y123
$YBa_2Cu_3O_{7-\delta}$

Bi2212
"$Bi_2Sr_2CaCu_2O_8$"

110 K Superconductor



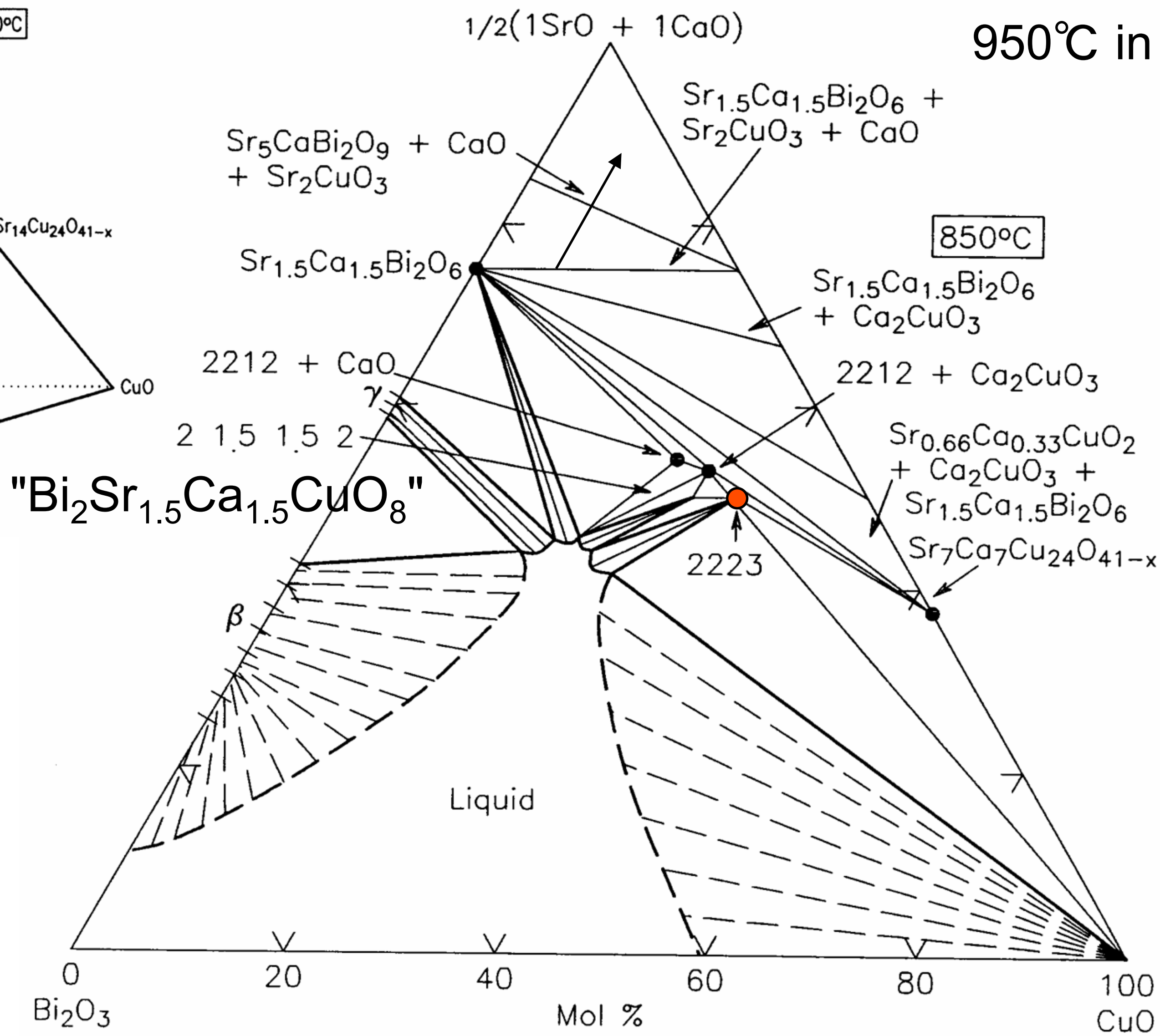
Phase diagram in the Bi-Sr-Ca-Cu-O system



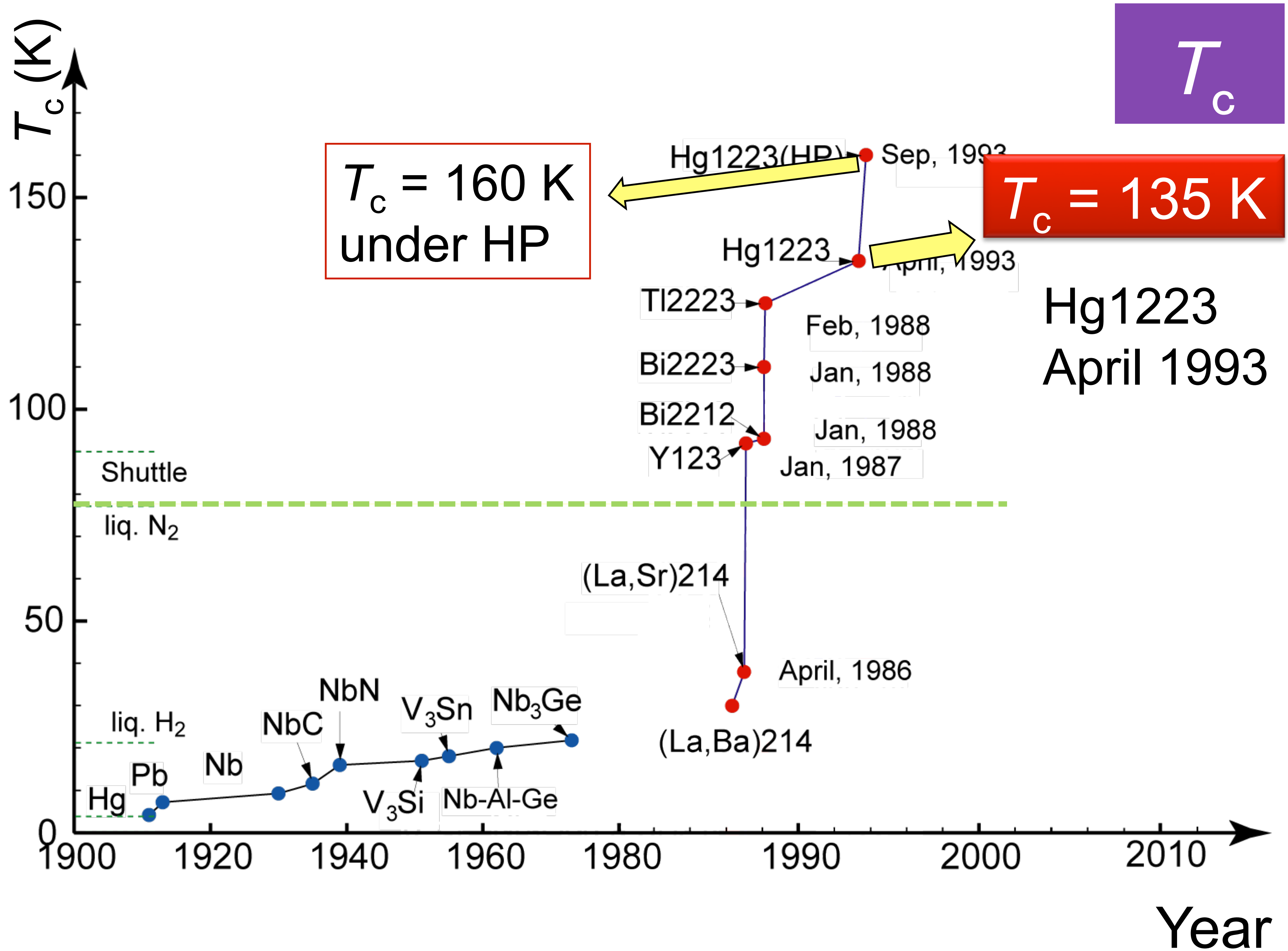
Bi2212

Bi2223

950℃ in air



P. Majewski, et al., Adv. Mater. 3, 67 (1991)



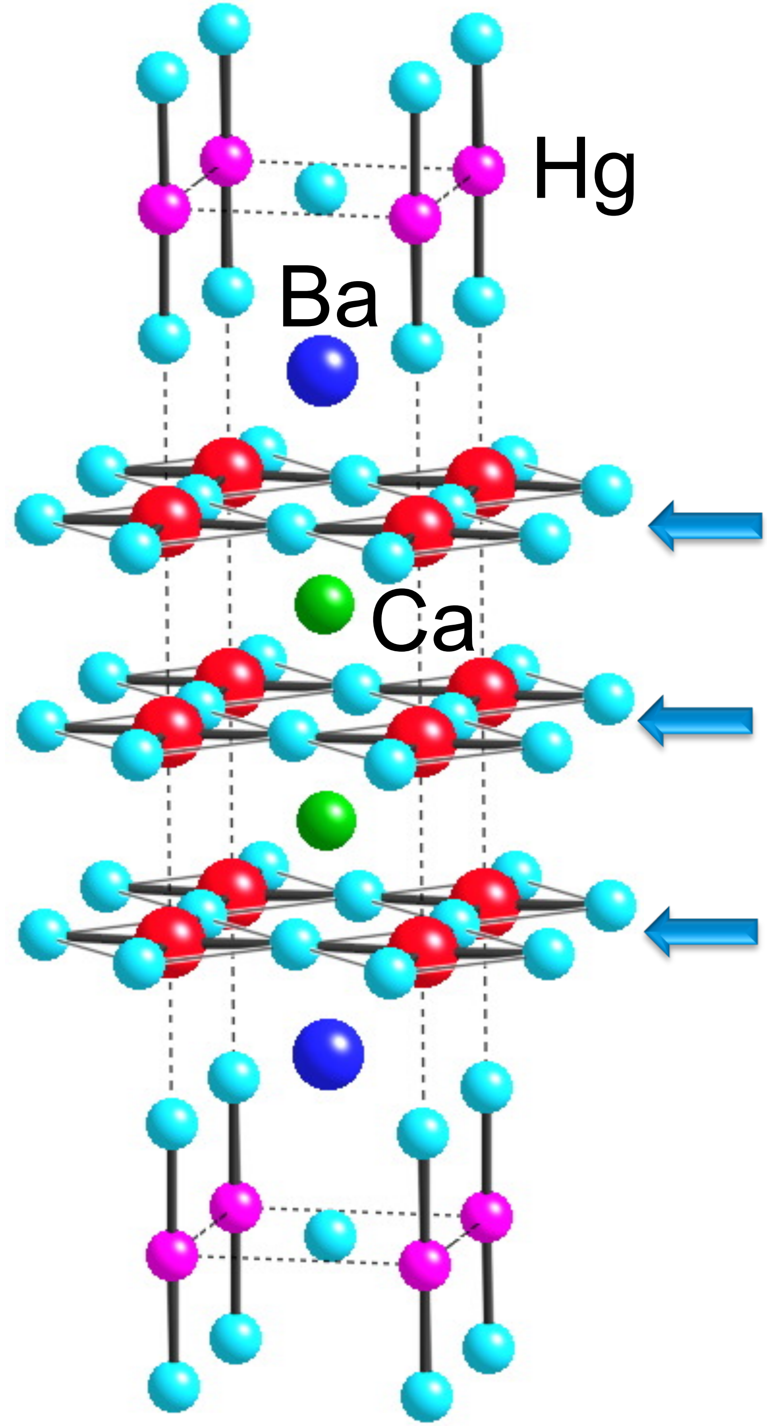
T_c
T_c = 160 K under HP
T_c = 135 K
Hg1223
April 1993
T_c (K)
150
100
50
0
Year
1900
1920
1940
1960
1980
1990
2000
2010
Hg1223(HP)
Sep, 199
Hg1223
1993
Tl2223
Feb, 1988
Bi2223
Jan, 1988
Bi2212
Jan, 1988
Y123
Jan, 1987
Shuttle
liq. N_2
(La,Sr)214
April, 1986
(La,Ba)214
liq. H_2
Hg
Pb
Nb
NbC
NbN
V_3Si
V_3Sn
Nb-Al-Ge
Nb_3Ge

Ultimate HTSC

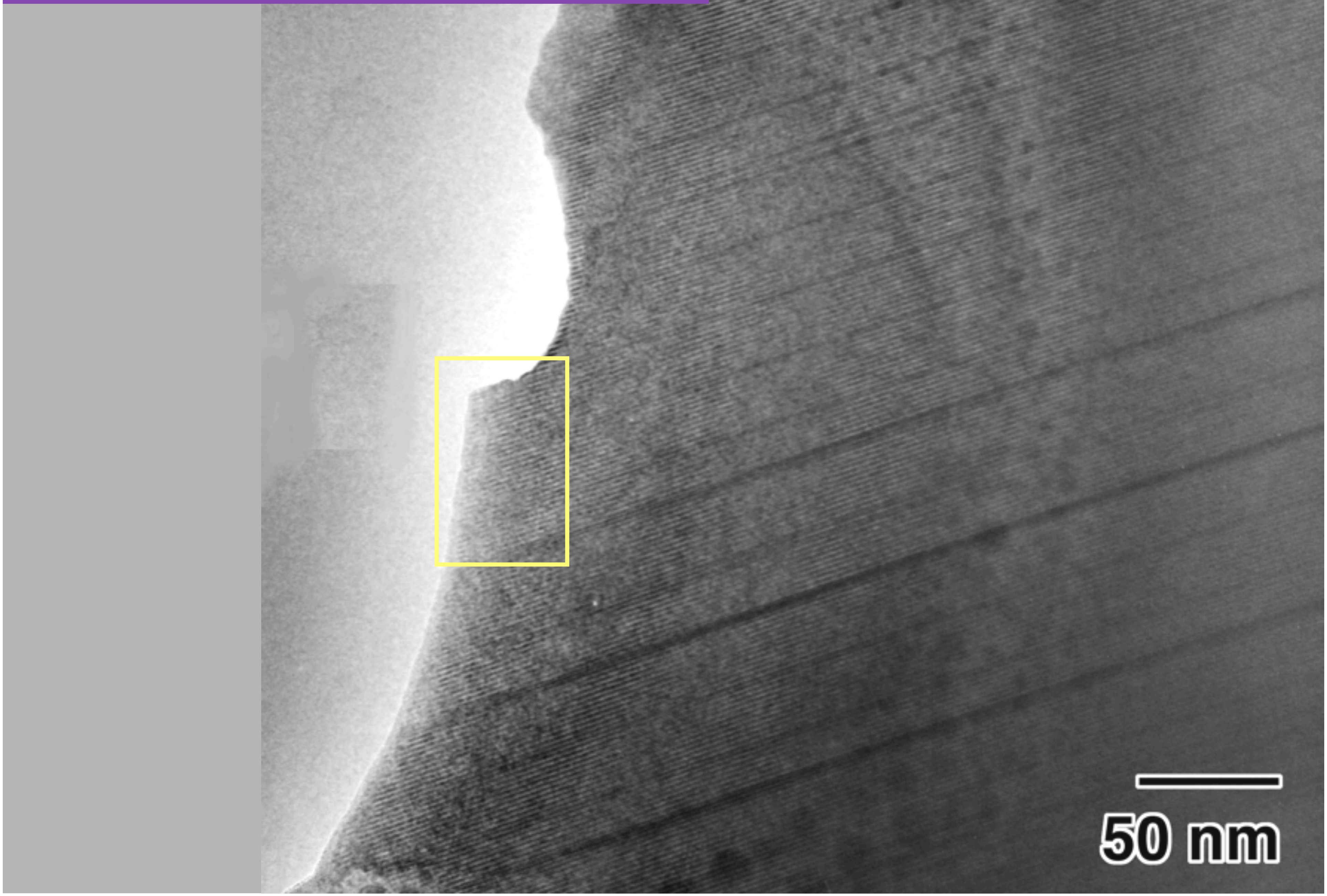
Hg1223
$HgBa_2Ca_2Cu_3O_{8+\delta}$

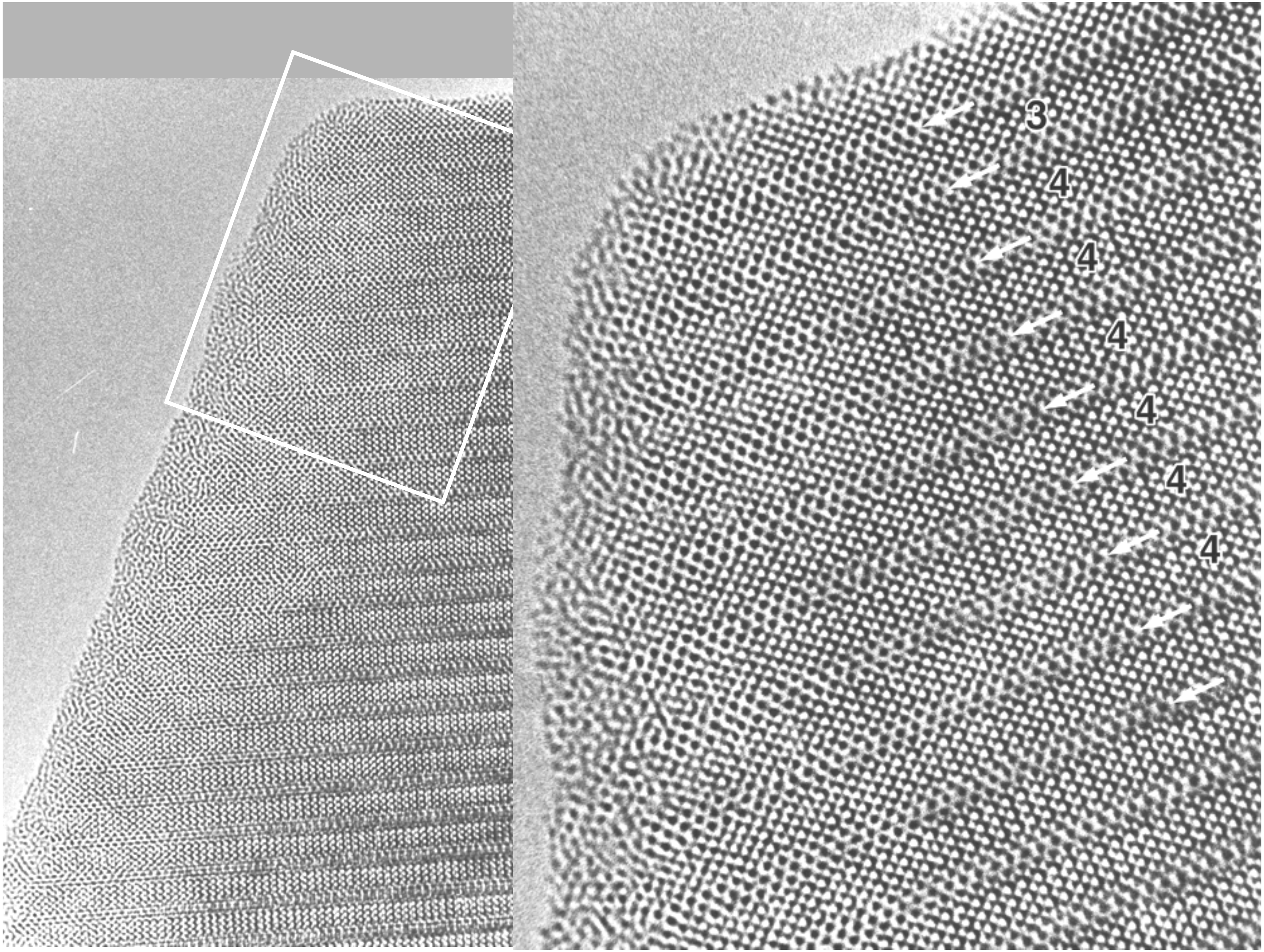
World record T_c:
135 K @ AP
160 K @ HP

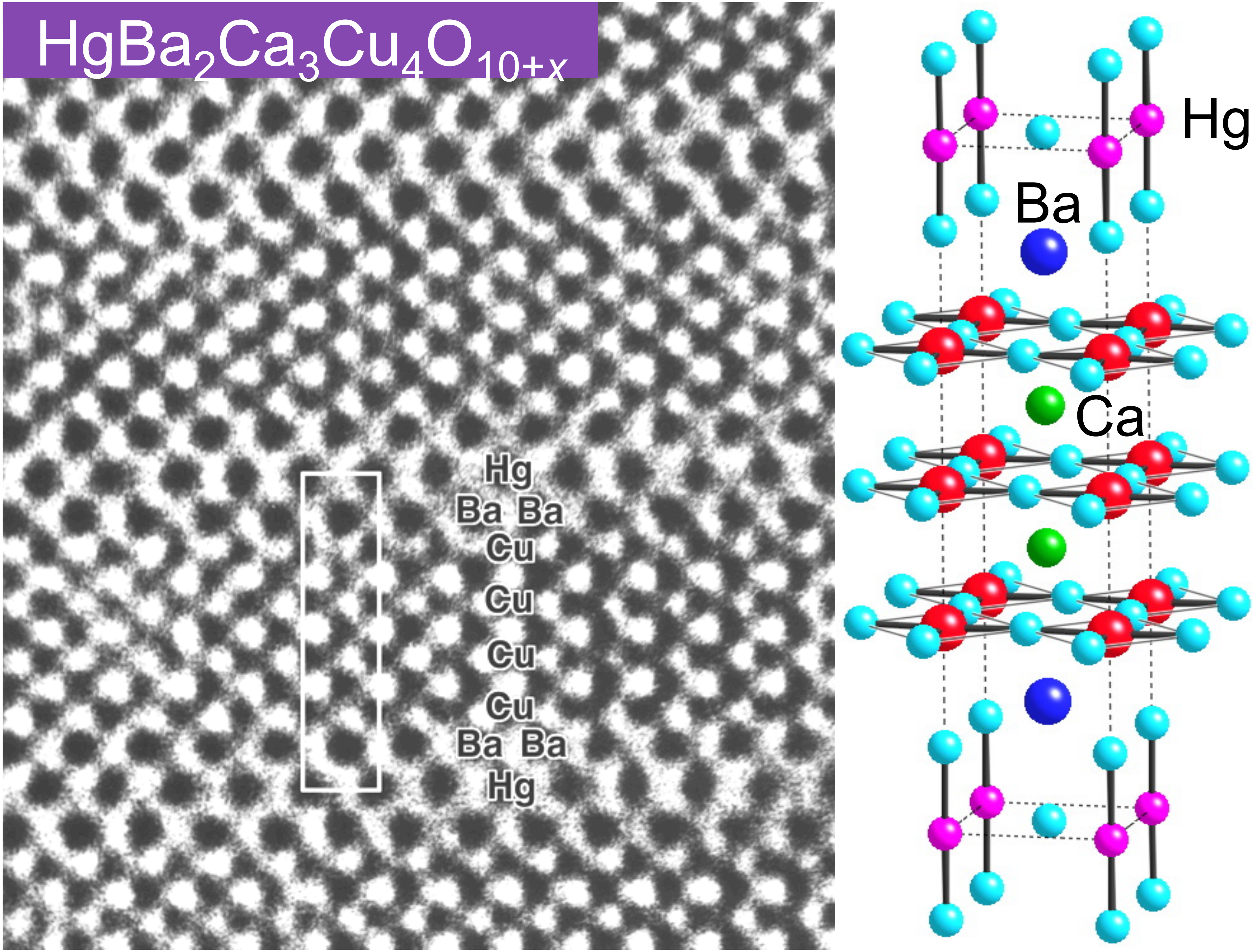
with a beautiful
crystal structure



Electron Microscopy




3
4
4
4
4
4
4


$HgBa_2Ca_3Cu_4O_{10+x}$
Hg
Ba Ba
Cu
Cu
Cu
Cu
Ba Ba
Hg
Hg
Ba
Ca

HTSC: plate crystals

Hiroi, Shohei

晶平

crystal plate

Outline

- Introduction to superconductivity
- Copper oxide superconductors:
  Preparation and Materials
- Mechanism of the superconductivity
- What determines the T_c?
- Future prospect

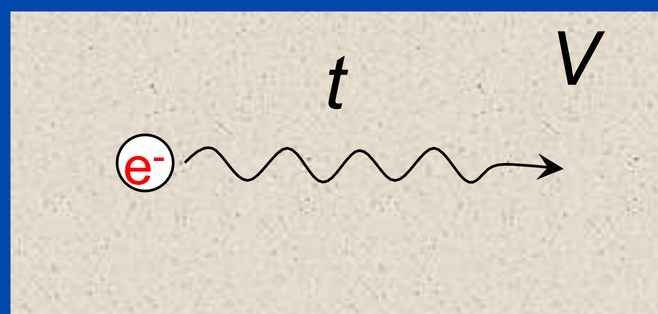
Beyond the Band Picture

Free electrons + periodic potential from ions

= Bloch electrons

Mean-field or one-electron approximation assumes uniform potential *V* from other electrons.

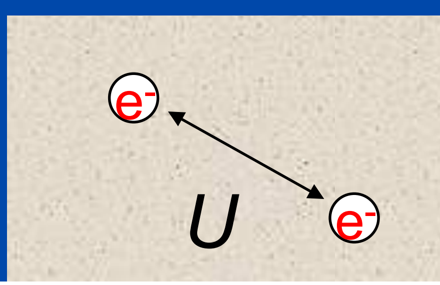
⇒ nearly free electrons with effective mass *m**.



t: kinetic energy

$t \propto W$: bandwidth

However, electrons are not completely free, but there is always Coulomb repulsion between them.

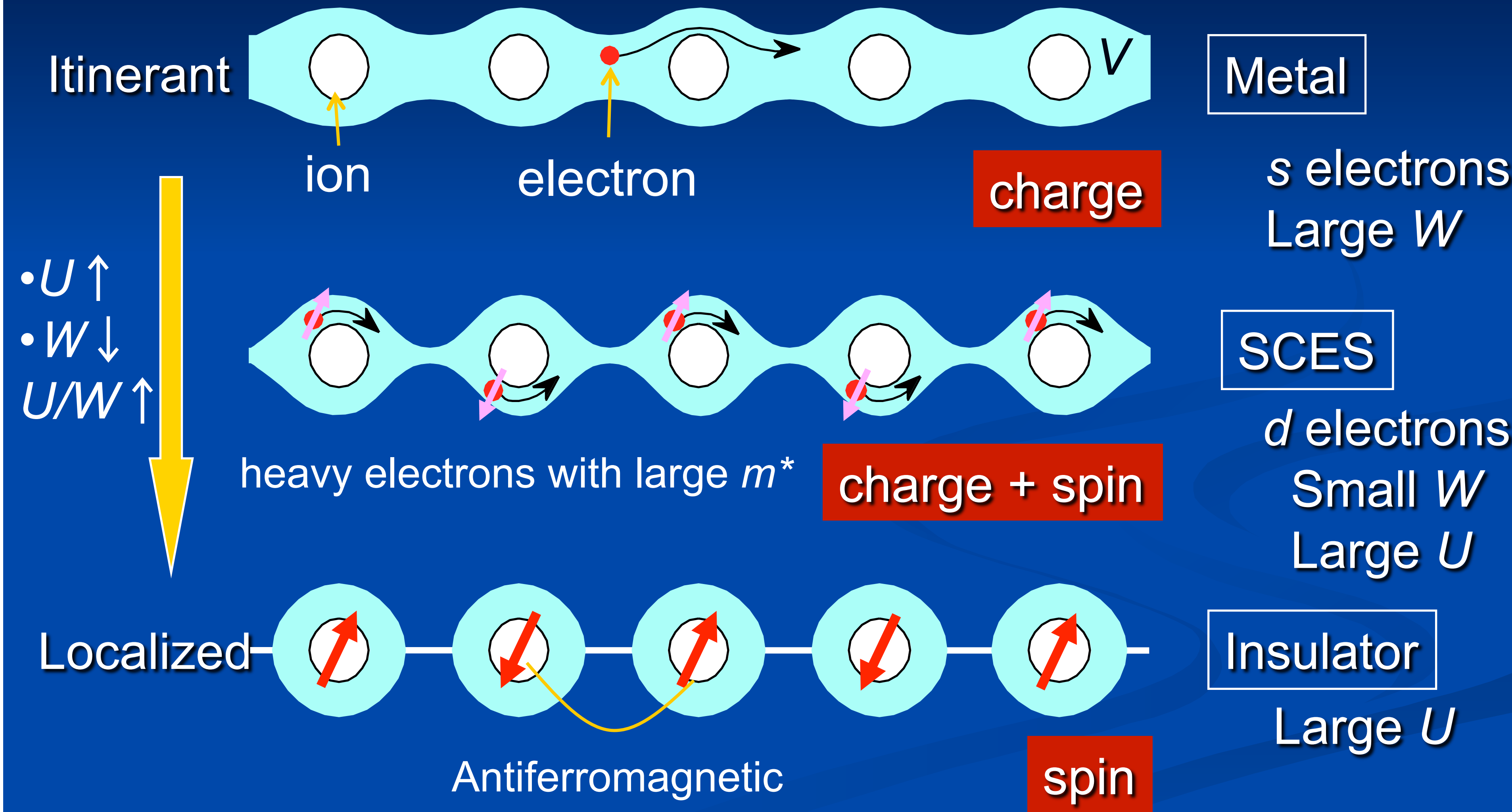


U: Coulomb repulsion or electron correlation

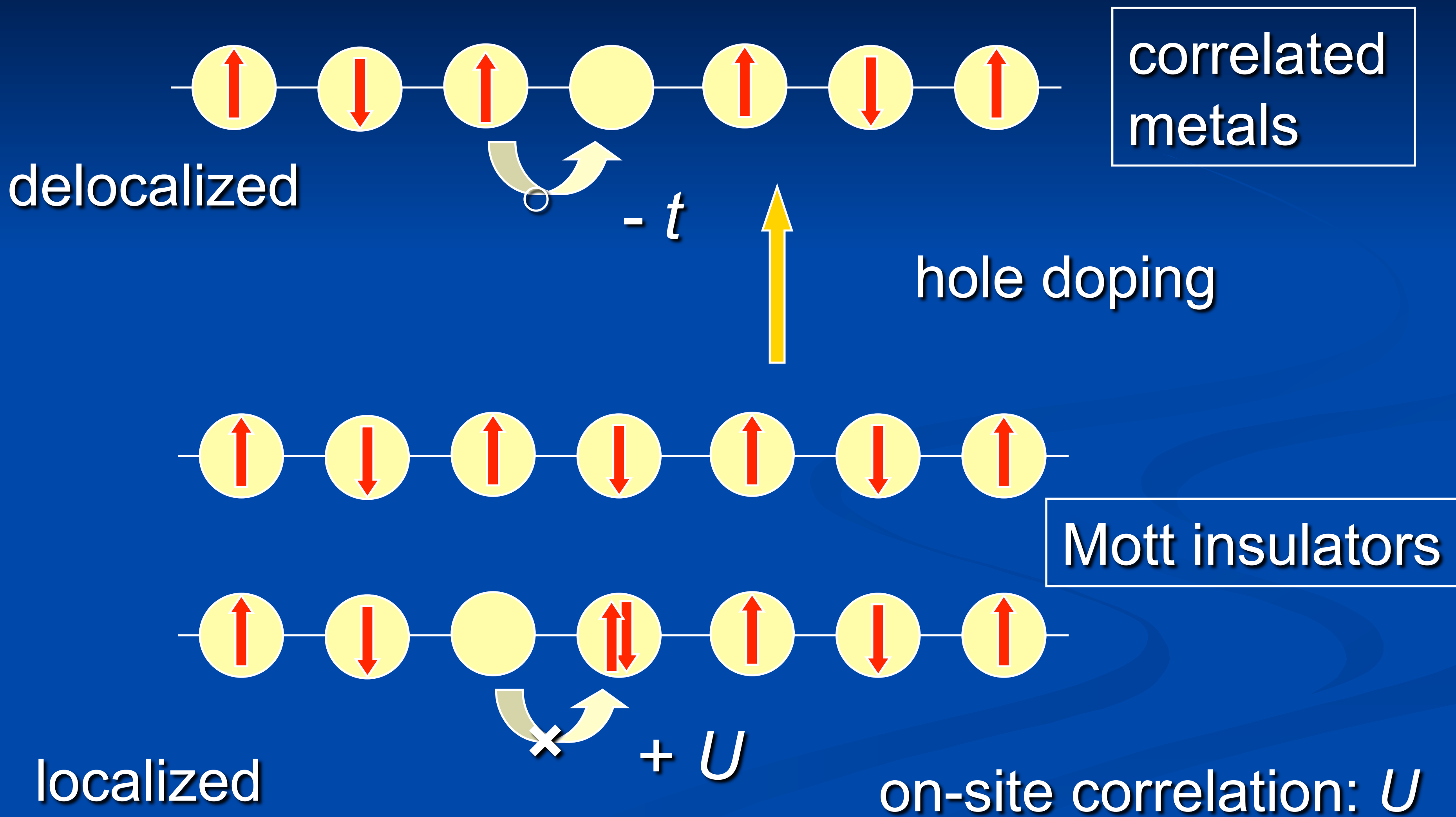
W* vs. *U

Strongly correlated electron system: SCES

Electron correlation *U* vs. Bandwidth *W*



Strongly correlated electron systems



What determines the T_c?

Superconductivity = electron pairs (Cooper pairs)

$$T_c = \underline{\omega} \underline{\exp\left(-\frac{1}{\lambda}\right)}$$

An excitation to generate pairing "glue"

damping factor ~ 0.1

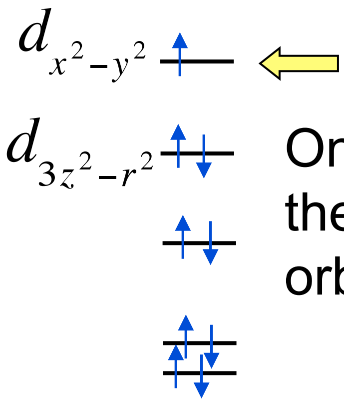
Phonon : $\omega = \omega_{ph}$ ~ 300 K ⇨ T_c ~ 300×0.1 = 30 K

"BCS wall"

What is the glue for copper oxides?

Copper oxides

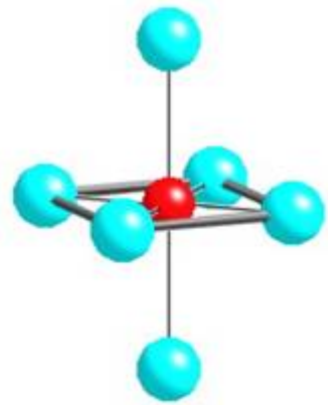
$Cu^{2+}O_4$ square with an S = 1/2 spin is a motif to build up various types of low-dimensional structures!

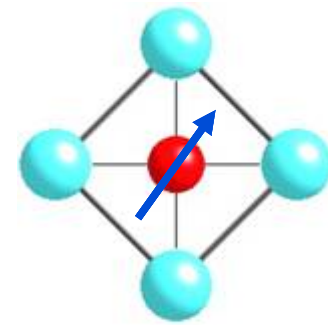


Cu^{2+}: $3d^9$

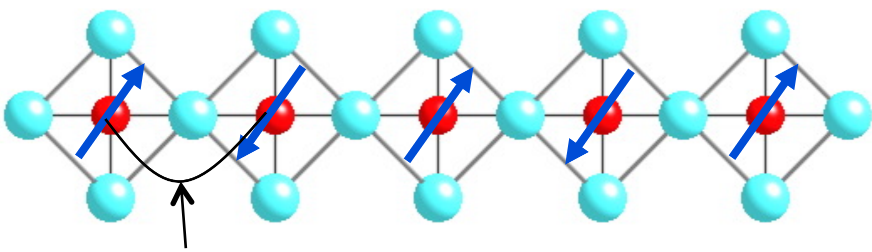
One electron/hole in the nondegenerate orbital

very rare!





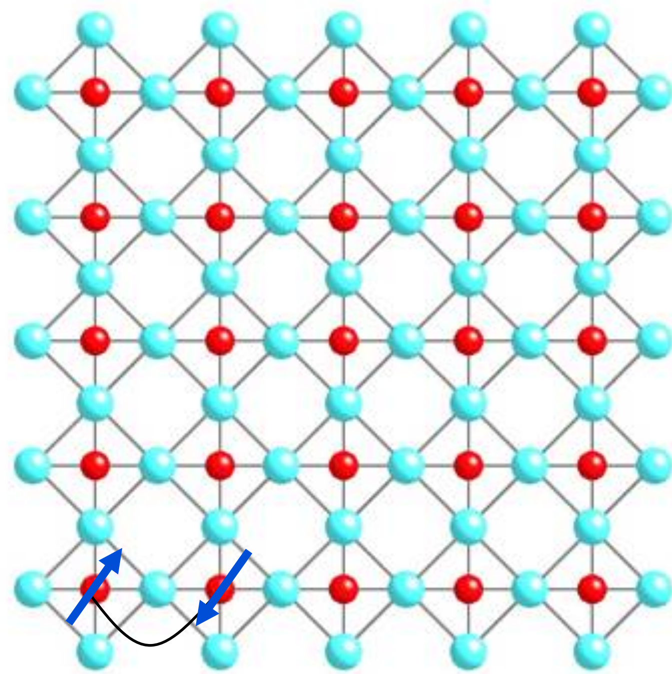
corner-sharing chain



J: antiferromagnetic coupling

J = 2,200 K

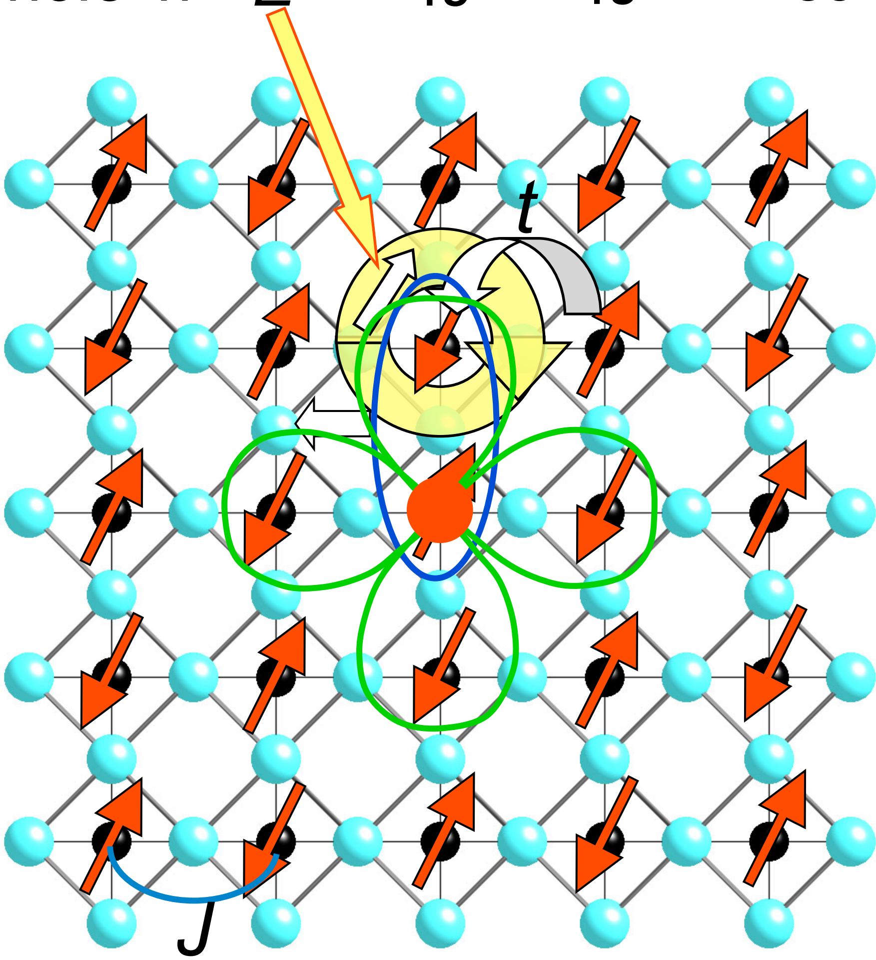
2D square lattice: CuO_2 plane



J = 1,500 K

Hole doping and HTSC in the CuO_2 plane

hole : h^+ $E = -4J \quad -4J \quad = -8J \rightarrow -7J$



localized quantum spins on the □ lattice

↓ hole doping

Zhang-Rice singlet

strongly correlated electron system

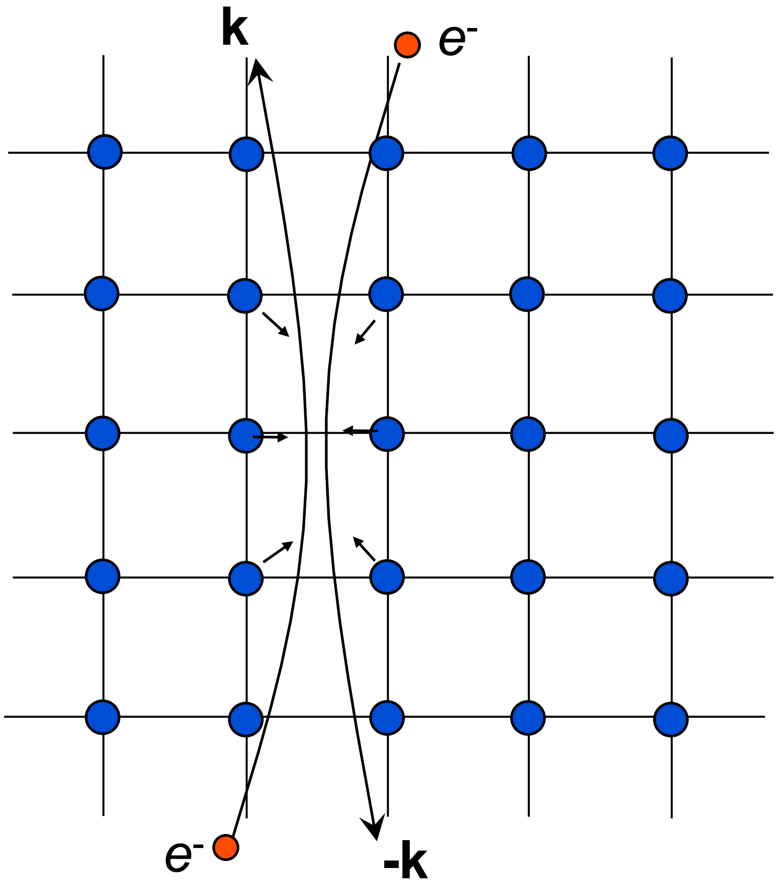
↓ a pair of Z-R singlets, Cooper pair

Superconductivity

hole pairs on oxygens in a spin liquid made of Cu spins

Mechanisms of the superconductivity

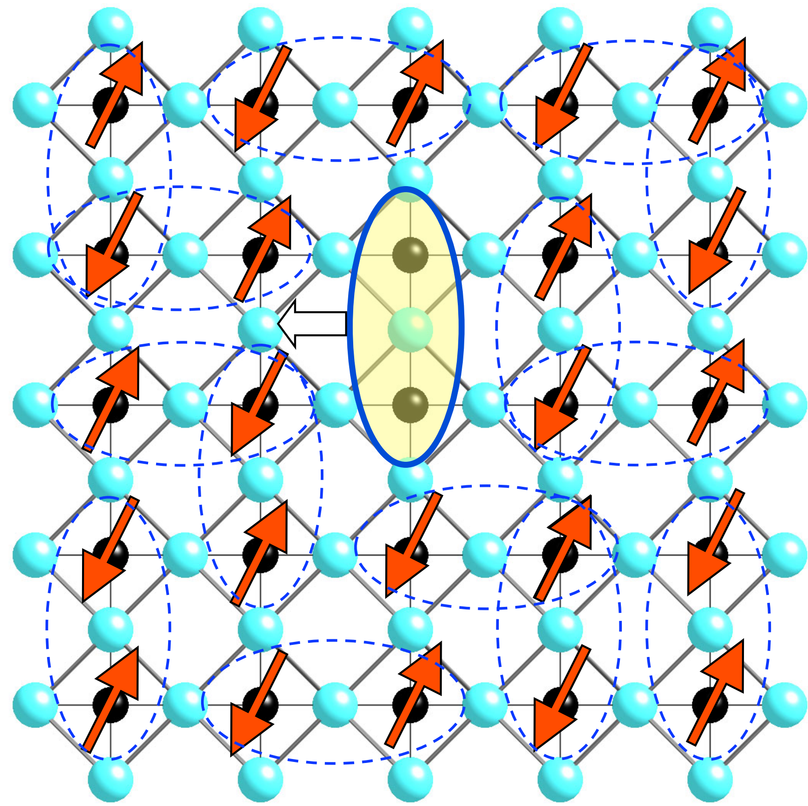
phonons in any lattice



k-space pairing

$T_c \propto \omega_{ph} \sim \omega_D \sim 300$ K

spins in the CuO_2 plane



real-space pairing?

$T_c \propto \langle J \rangle$: $J \sim 1{,}500$ K

What determines the T_c?

$T_c \propto$ Binding energy of Cooper pairs

$$T_c = \underline{\omega} \underline{\exp\left(-\frac{1}{\lambda}\right)}$$

Energy of relevant excitations

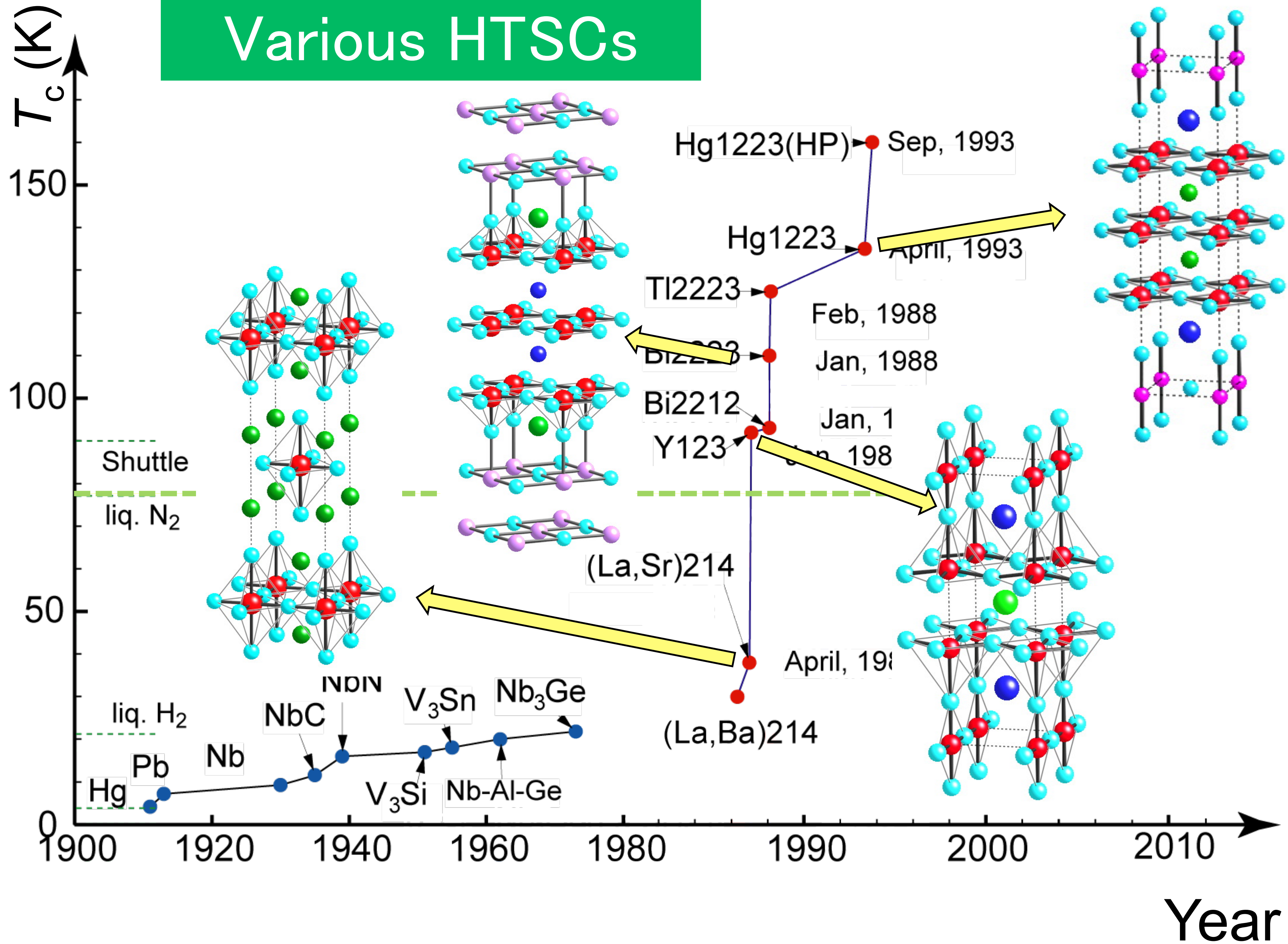
Damping factor

Maximum T_c

Phonon : $\omega = \omega_{ph} \longrightarrow T_c \sim 400 \times 0.1 = 40$ K

Antiferromagnetic interaction : $\omega = J$ ⇨ $T_c \sim 1{,}500 \times 0.1 = 150$ K

Various HTSCs



Questions

What is a materials factor that decides the T_c?

Any way to get over the record?

What determines the T_c?

$T_c \propto$ Binding energy of Cooper pairs

$$\underbrace{T_c = \omega}_{}\underbrace{\exp\left(-\frac{1}{\lambda}\right)}_{\text{Damping factor}}$$

Energy of relevant excitations

Damping factor

<u>Maximum T_c</u>

Phonon : $\omega = \omega_{ph}$ $\longrightarrow$ $T_c \sim 400 \times 0.1 = 40$ K

Antiferromagnetic interaction : $\omega = J$ $\longrightarrow$ $T_c \sim 1{,}500 \times 0.1 = 150$ K

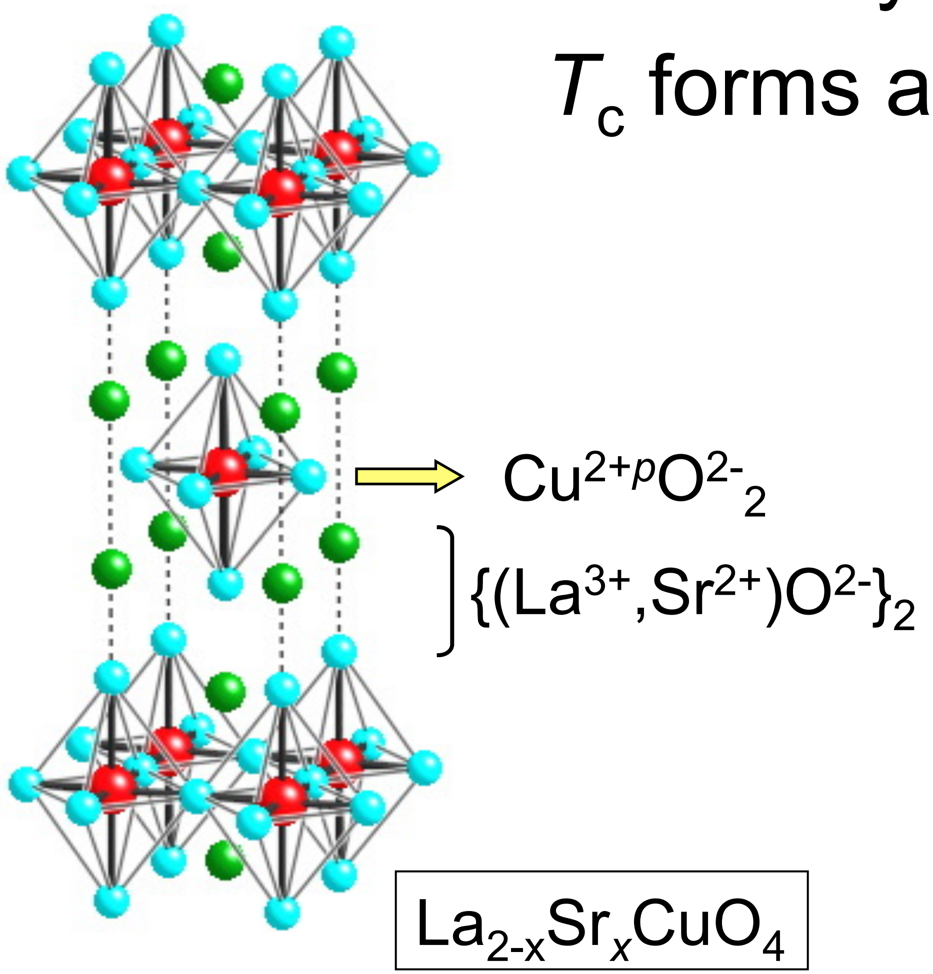
What is the damping factor for the copper oxides?

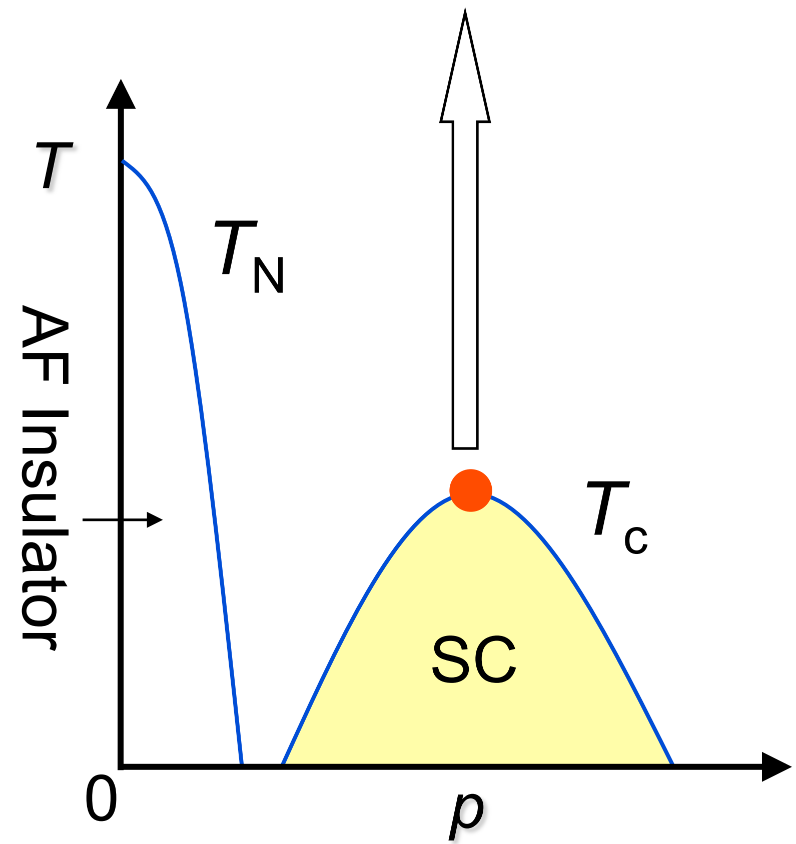
If doubled, T_c becomes room temperature!

What determines the T_c?

Hole density

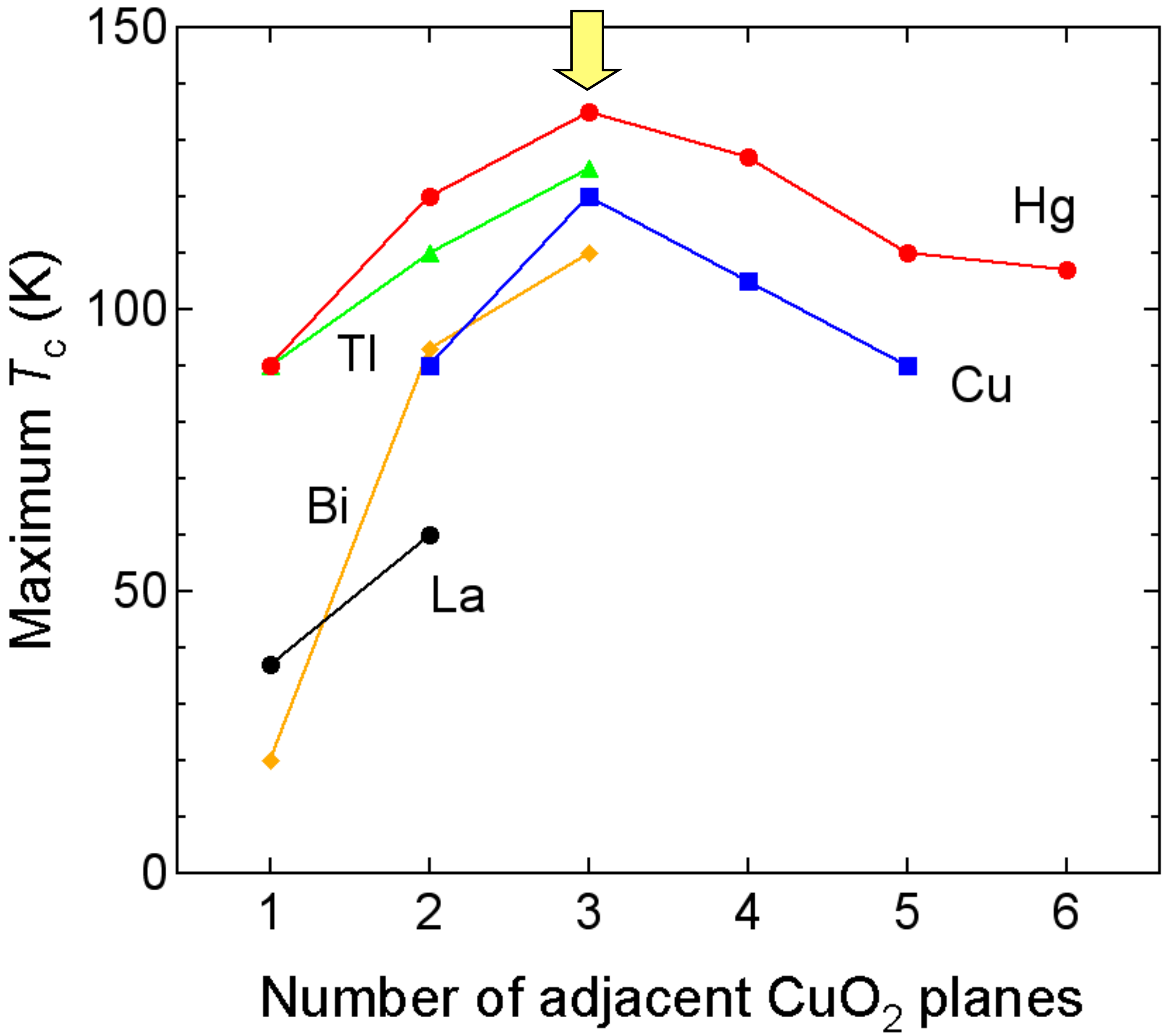
T_c forms a dome with a maximum.





T_c vs. number of CuO_2 planes

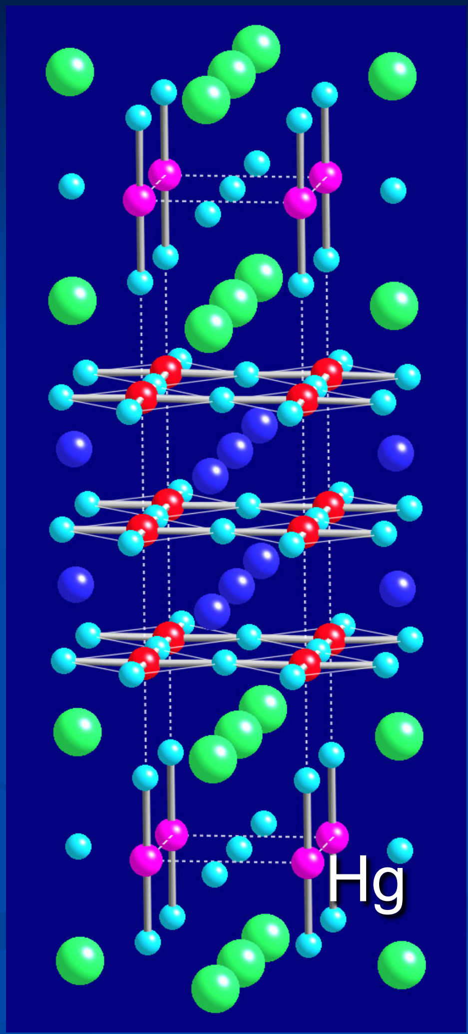
Always T_c reaches a maximum at three layers!



What determines the maximum T_c?

1. Apical oxygens, instead of number of CuO_2 planes

2. Randomness induced by chemical substitutions

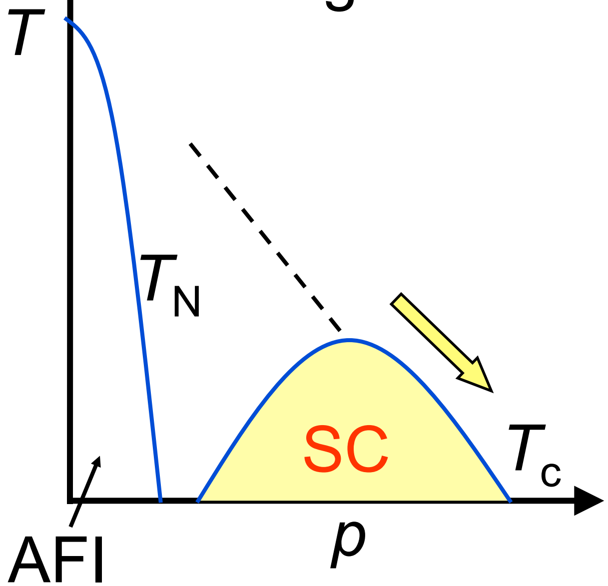


Hg1223

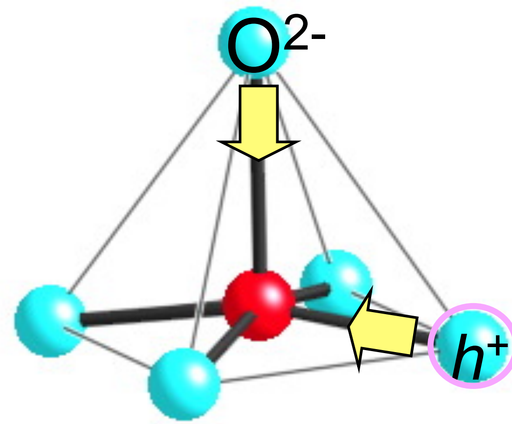
T_c dome: role of the apical oxygens

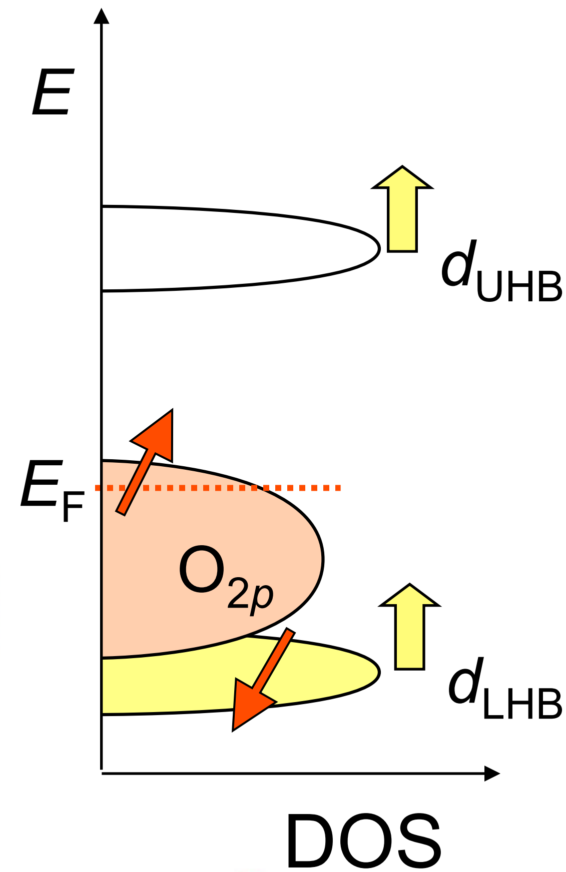
As the apical oxygen approaches to the CuO_2 plane, holes move from in-plane oxygen p orbital to Cu d orbital.

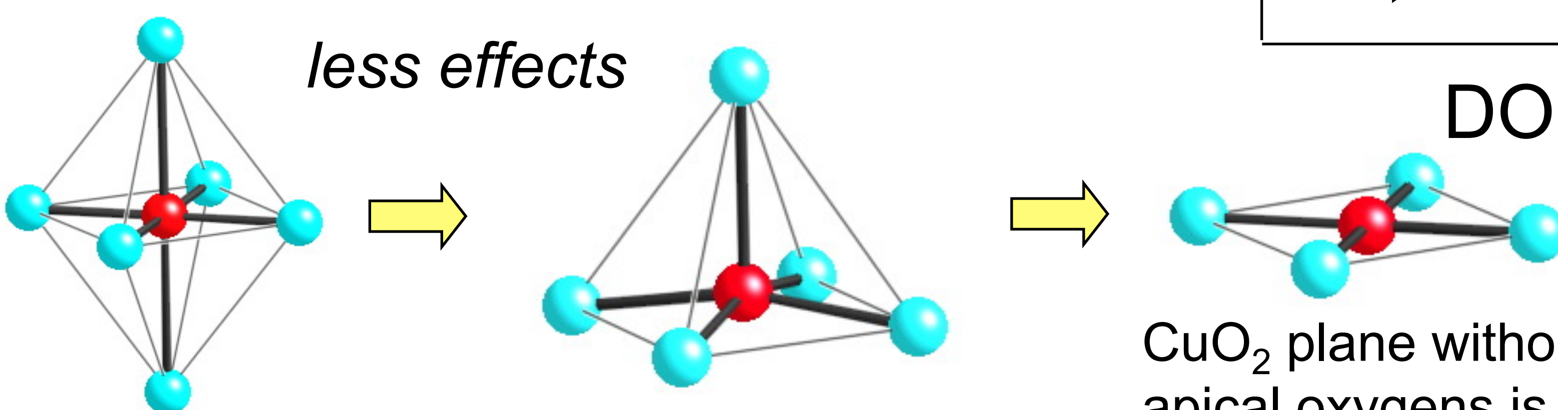
ZR singlets collapse to be just *d* holes.



apical oxygen

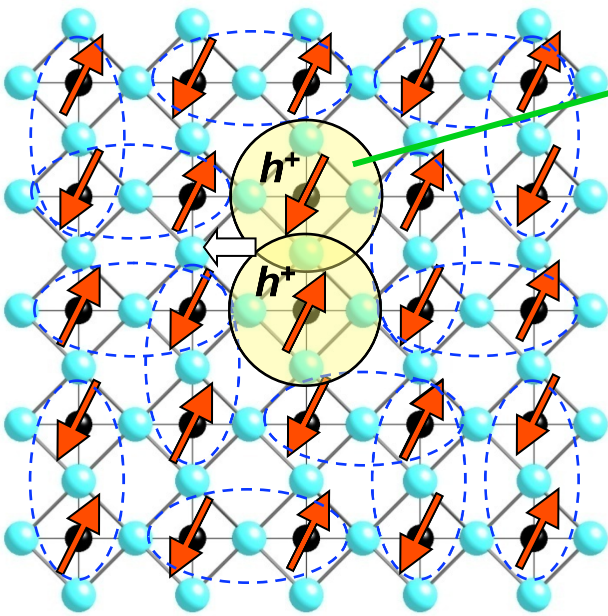




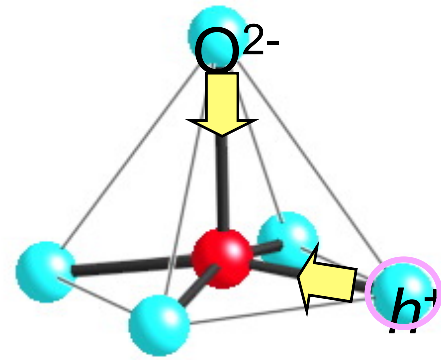


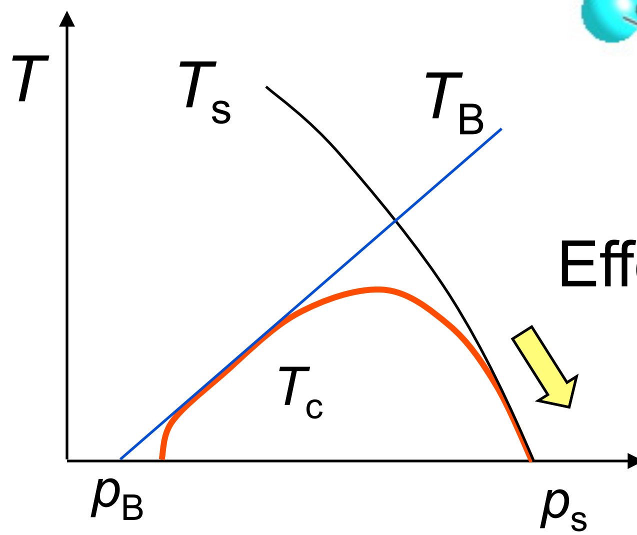
CuO_2 plane without apical oxygens is ideal.

T_c dome: role of apical oxygens



A pair of Zhang-Rice singlets is superconducting.

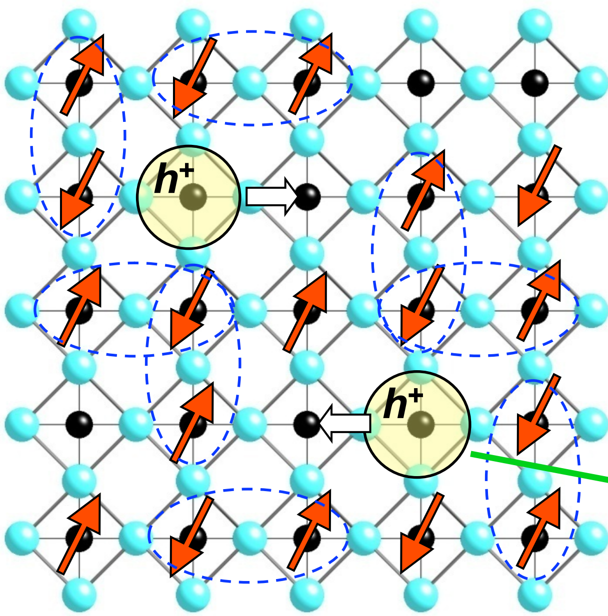




Effect of apical O

$p \uparrow$

$p' = p - p_B$



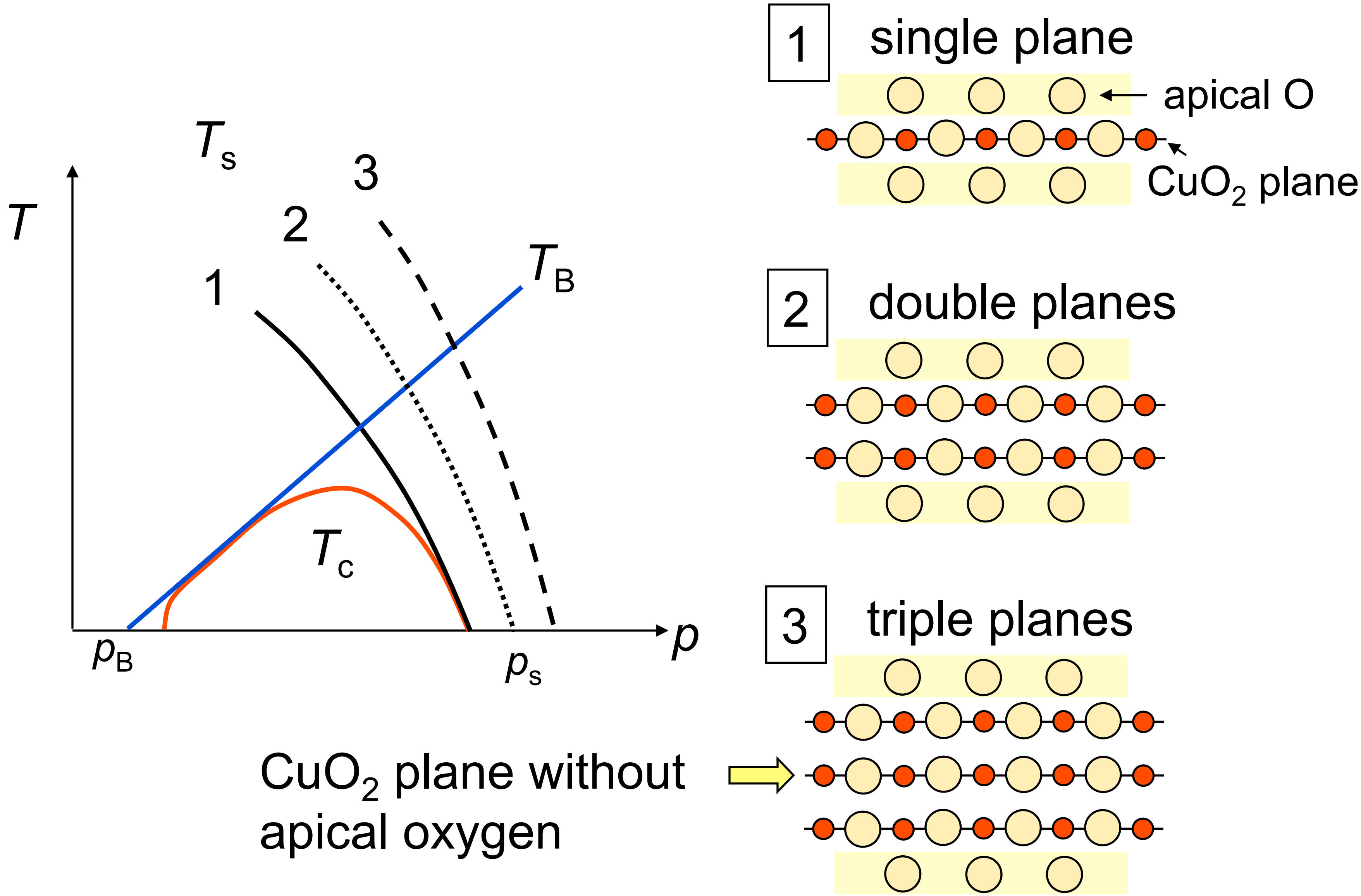
<u>Collapse of the background AF spin sea</u>

T_B: Bose condensation T for ZR singlets $\propto (\underline{p'/2})$

T_s: Binding energy from AF fluctuations

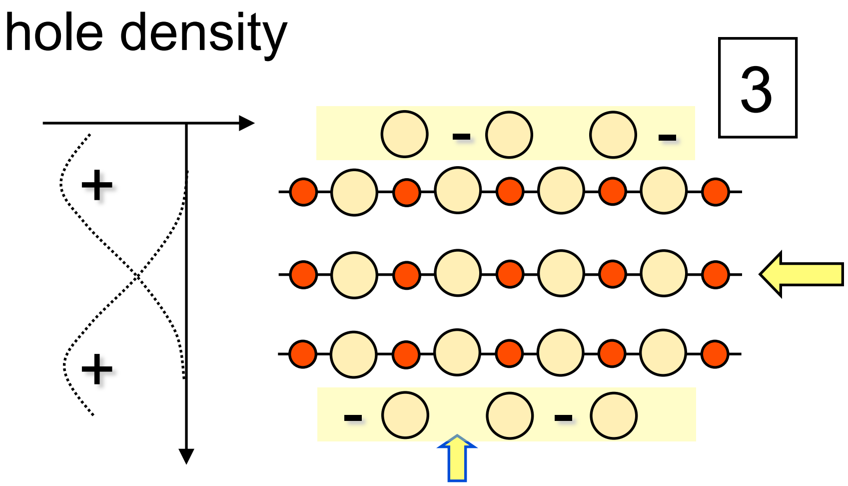
d holes
normal metal

T_c vs. number of CuO_2 planes



CuO_2 plane without apical oxygen

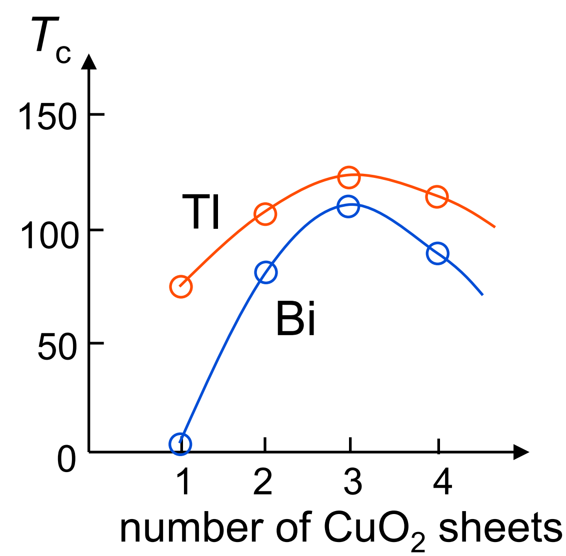
Further increasing the number of CuO_2 planes

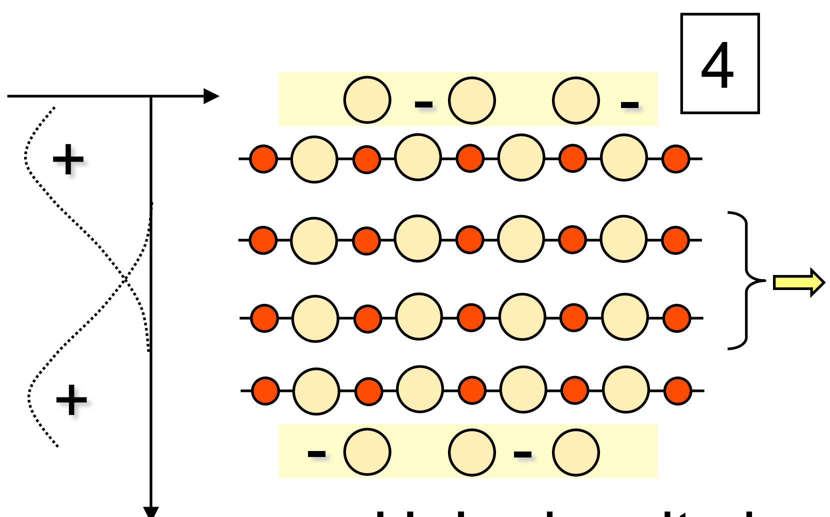


The middle plane can be doped optimally.

substituted metals or excess oxygens

Total number of holes there is limited.





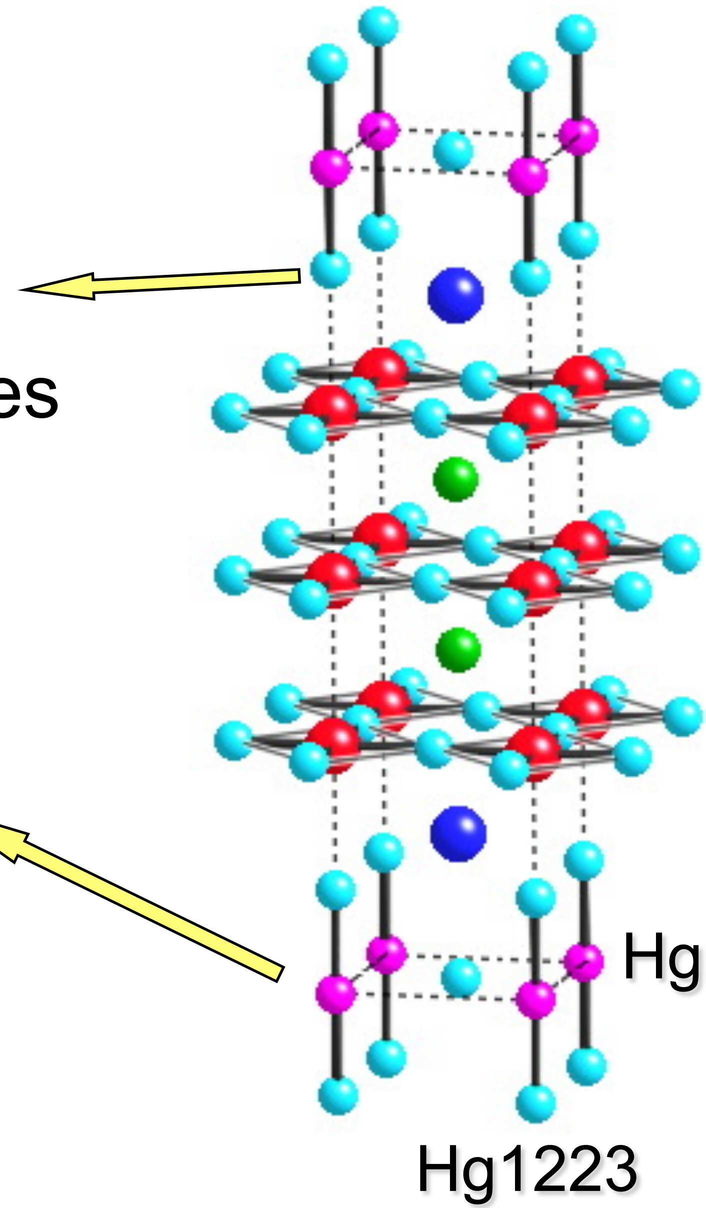
always underdoped!

Hole density is not enough for more planes.

What determines the maximum T_c?

1. Apical oxygens, instead of
   the number of CuO_2 planes

2. Randomness induced
   by chemical substitutions
   or excess oxygens



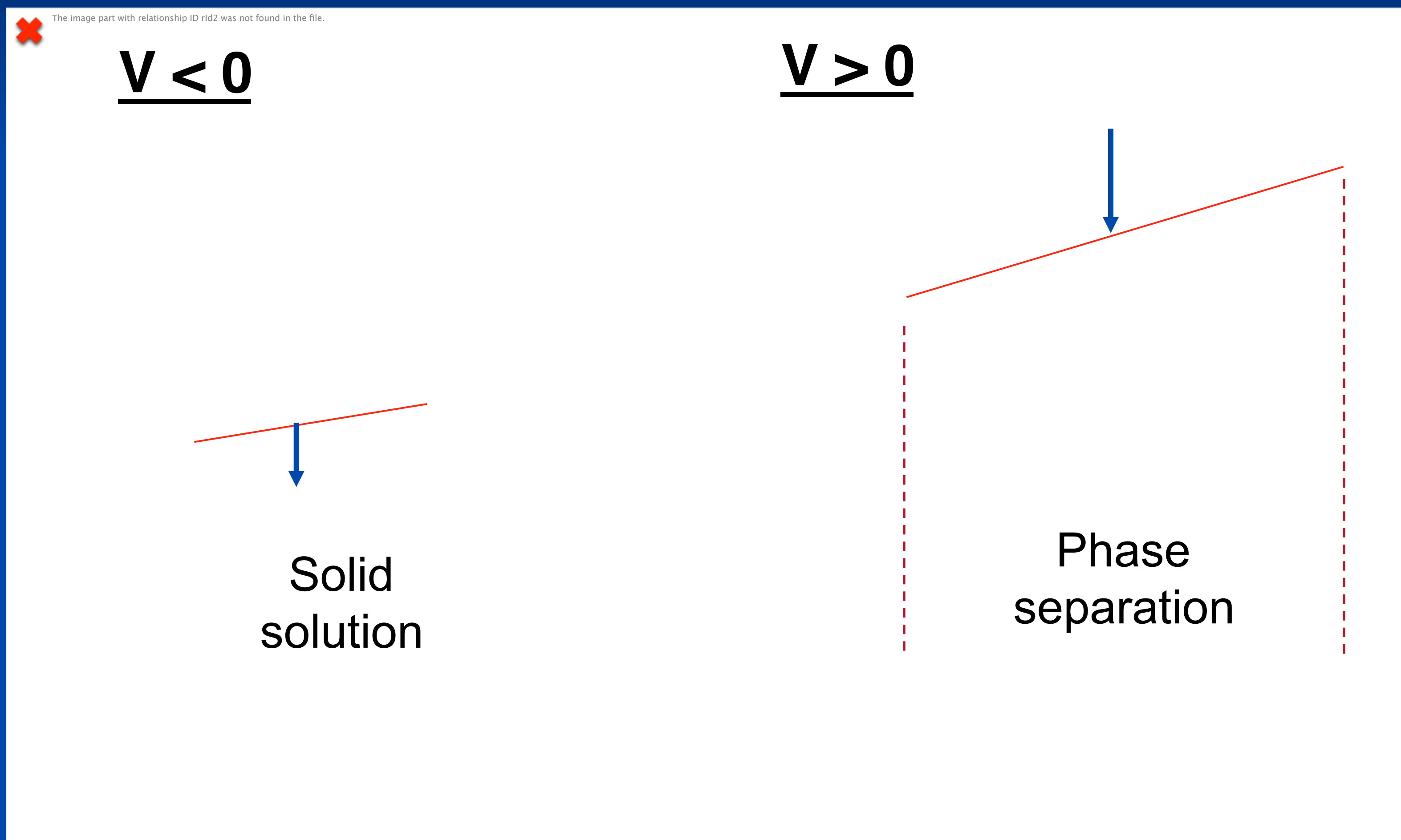
Thermodynamics of solid solutions

$$\boxed{F = E - TS}$$

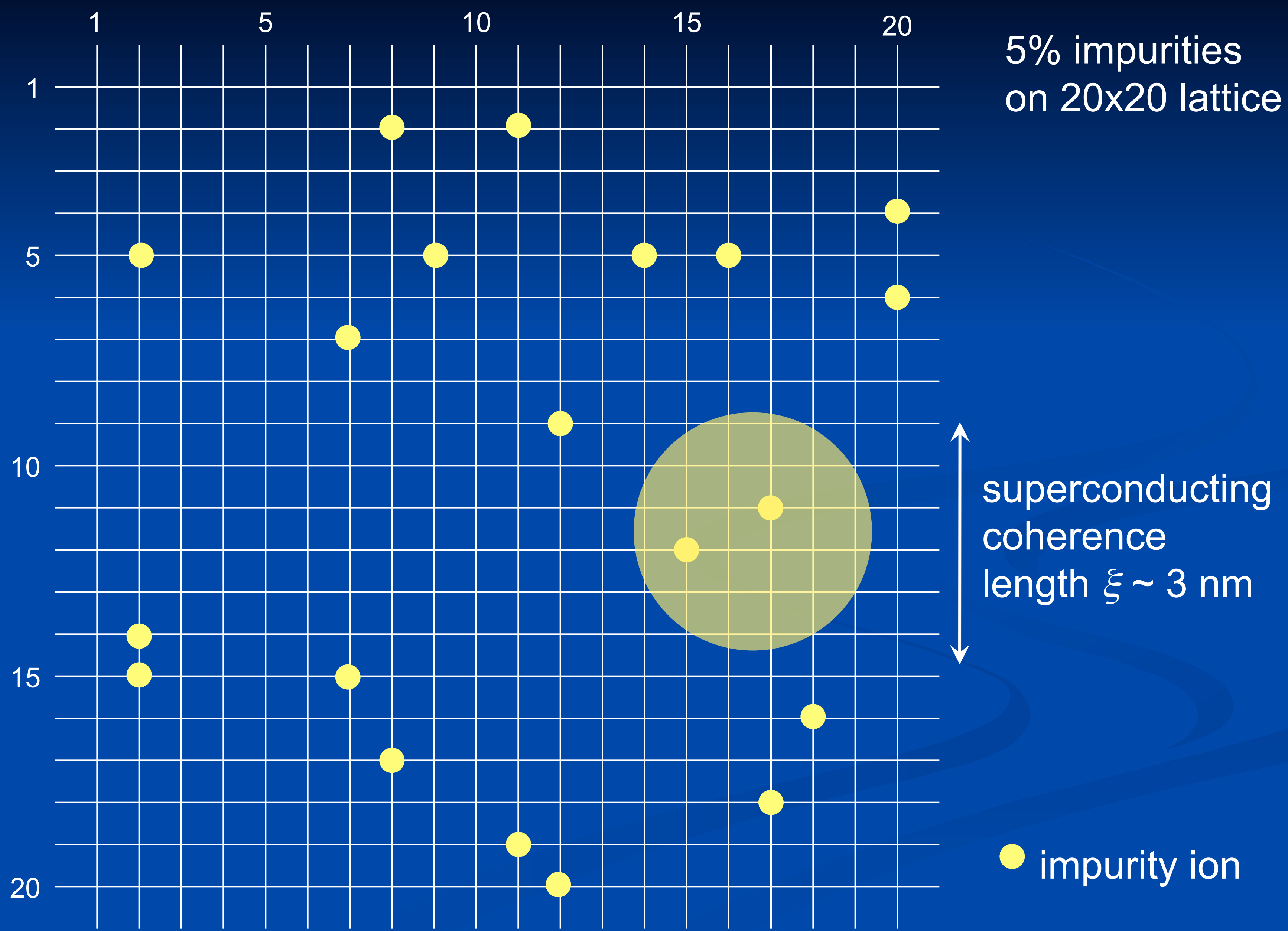
A-B phase diagram

$$E = Nz\{xV_{AA}+(1-x)V_{BB}+2x(1-x)V\}/2: \; V = V_{AB}-(V_{AA}+V_{BB})/2$$

$$-TS = Nk_B T\{x\ln x+(1-x)\ln(1-x)\}$$

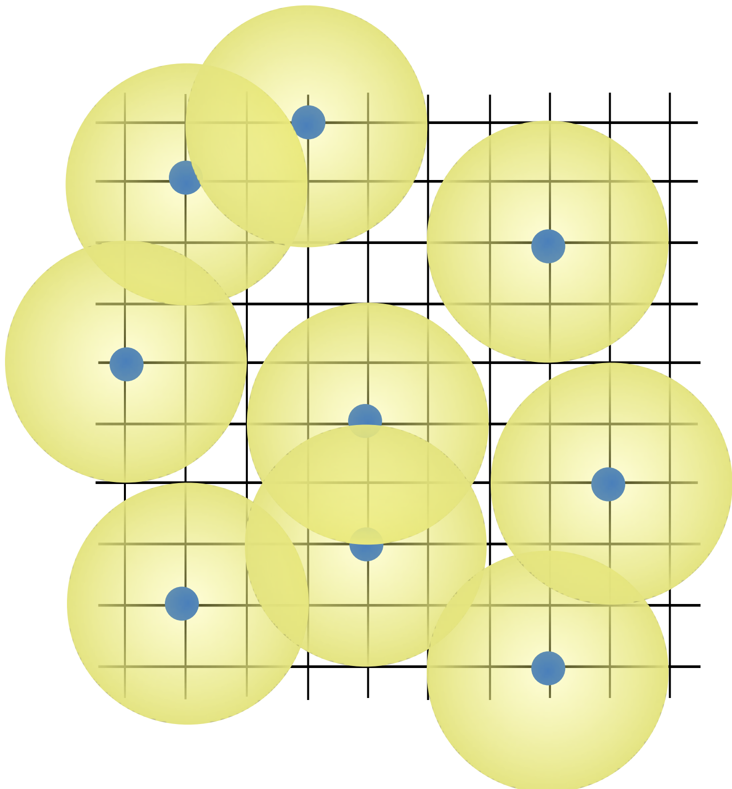


Random distribution of impurities



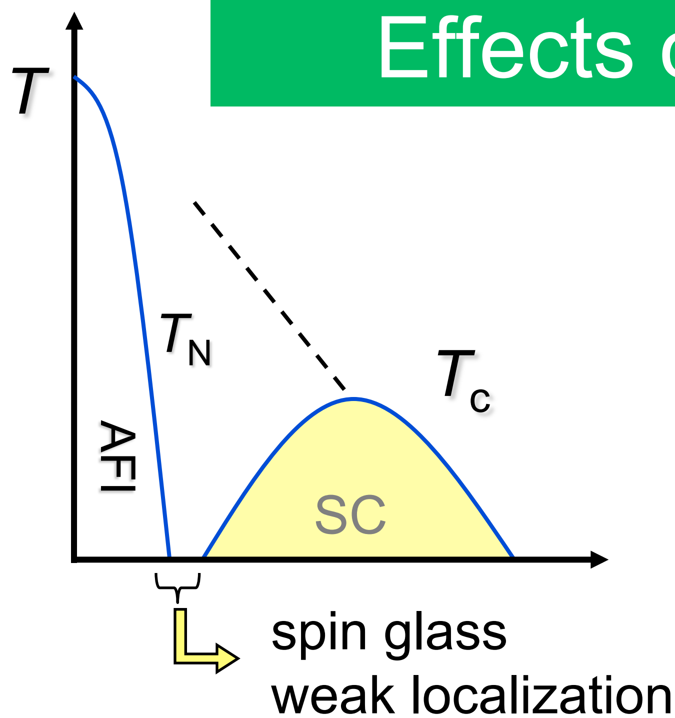
“Uniform” Solid Solutions

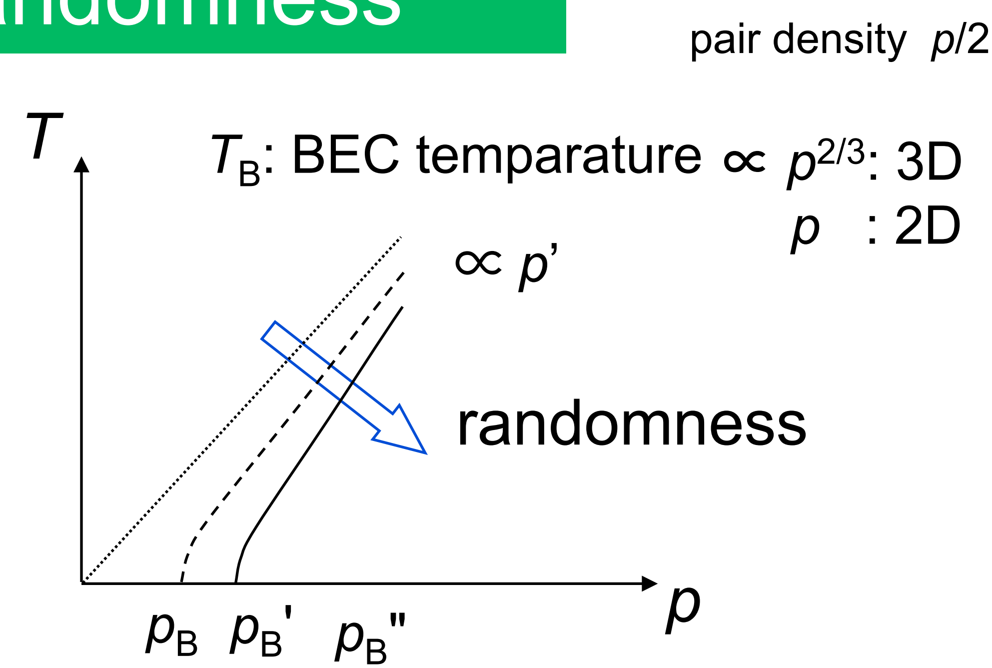
9 impurity ions on the 10x10 lattice



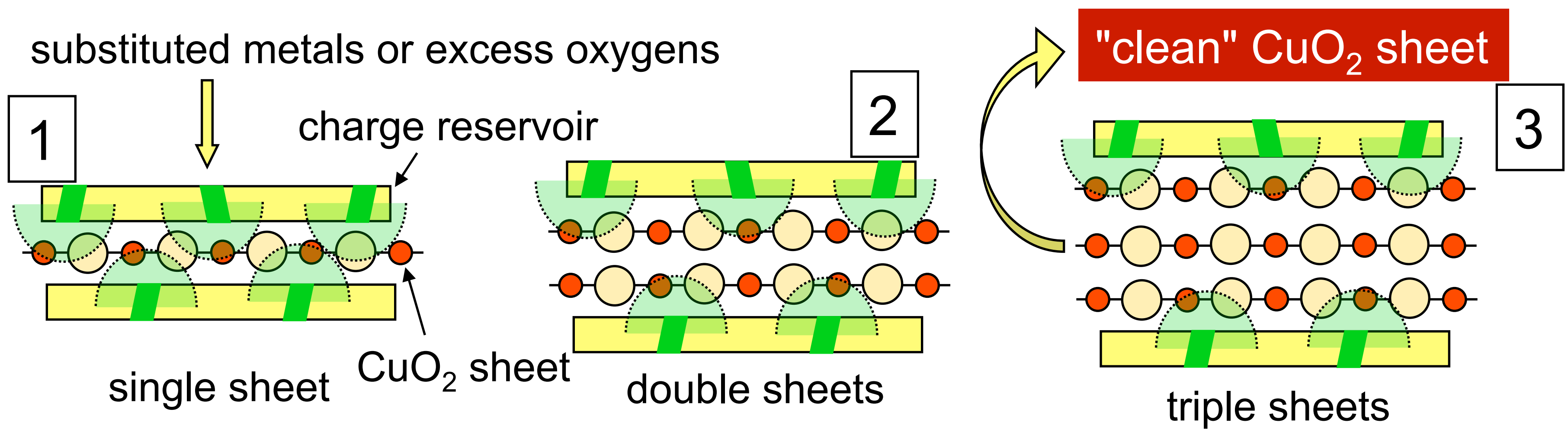
always results in an inhomogeneous distribution of impurities!

Effects of randomness



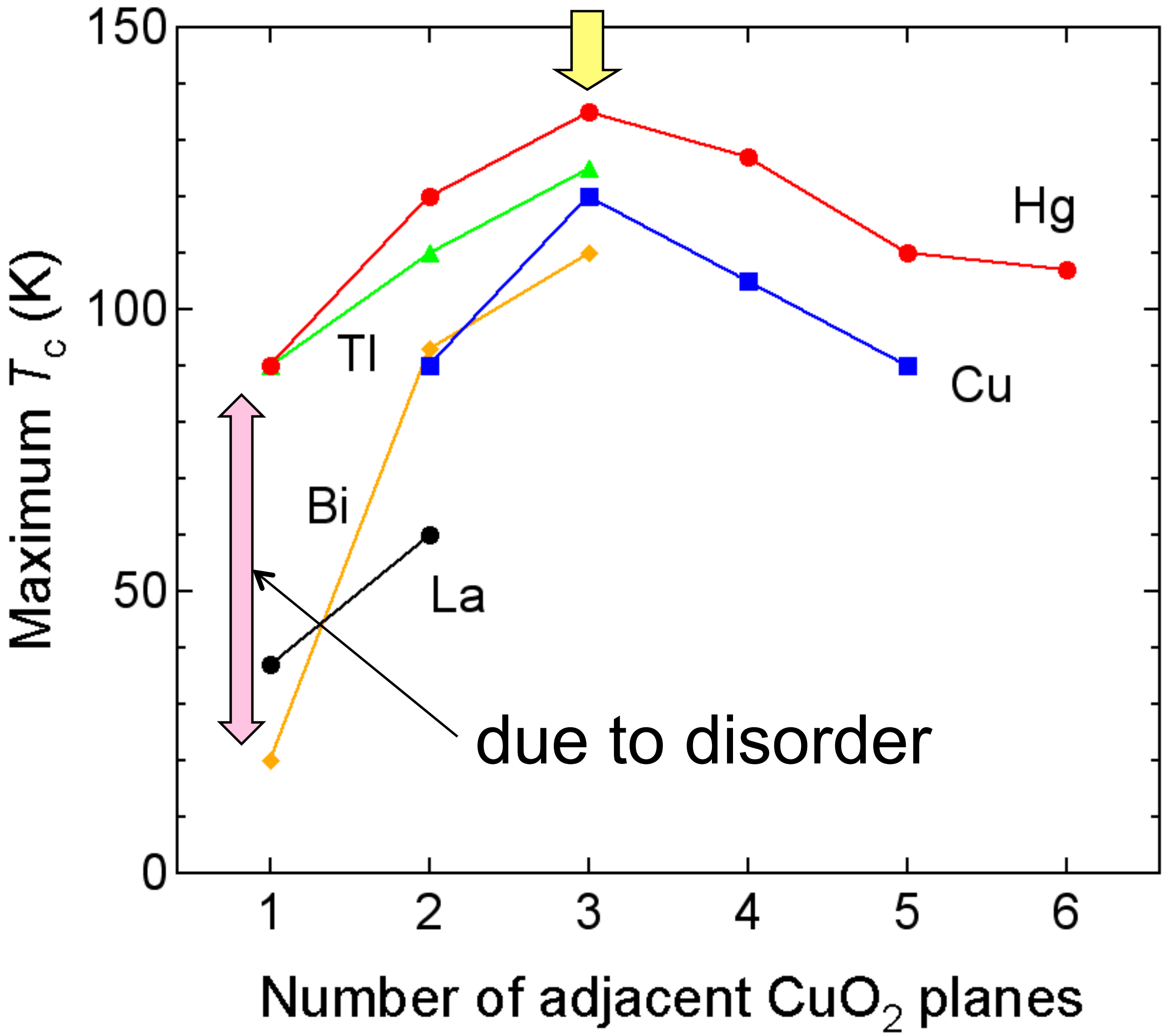


Some holes are trapped by the randomness and can not move.



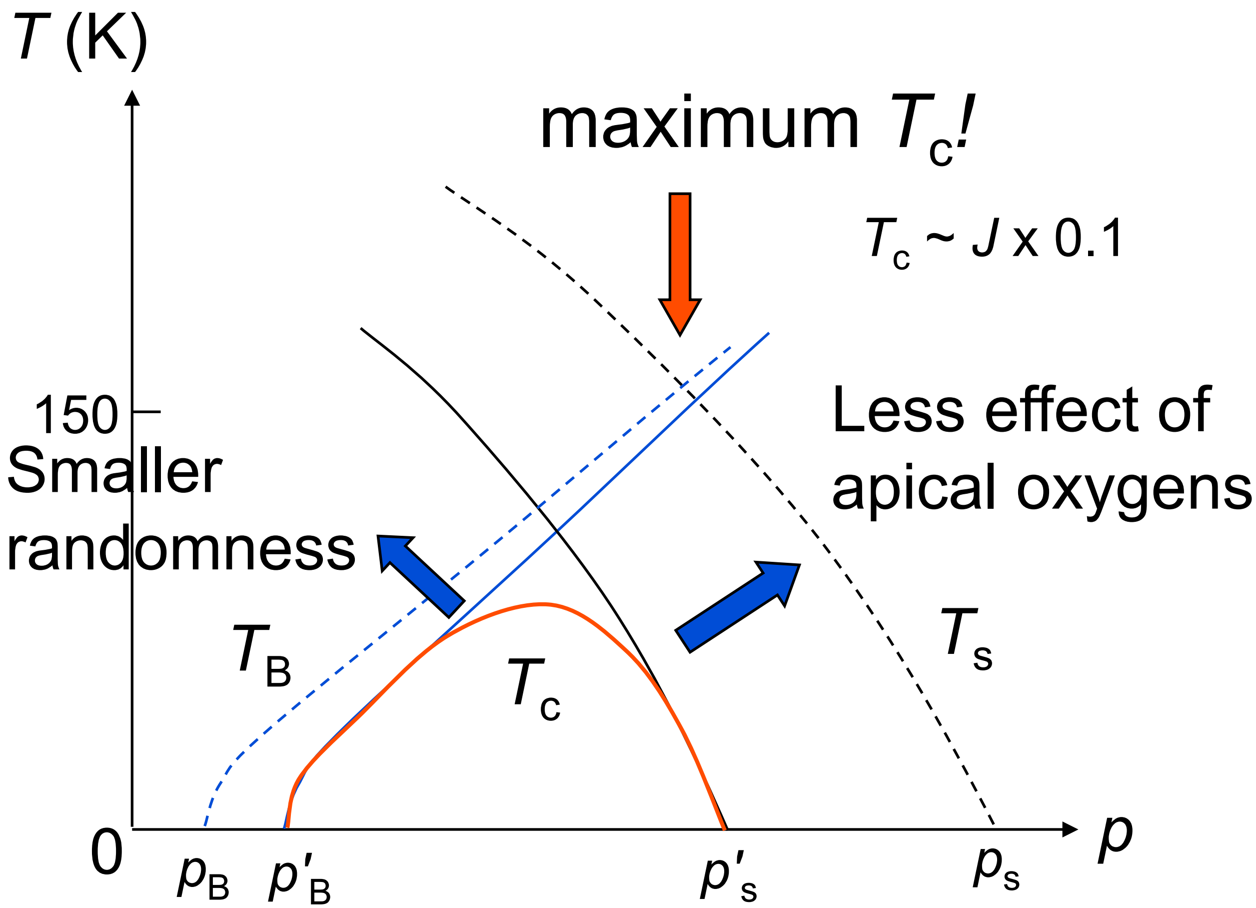
T_c vs. number of CuO_2 planes

Always T_c reaches a maximum at three layers!

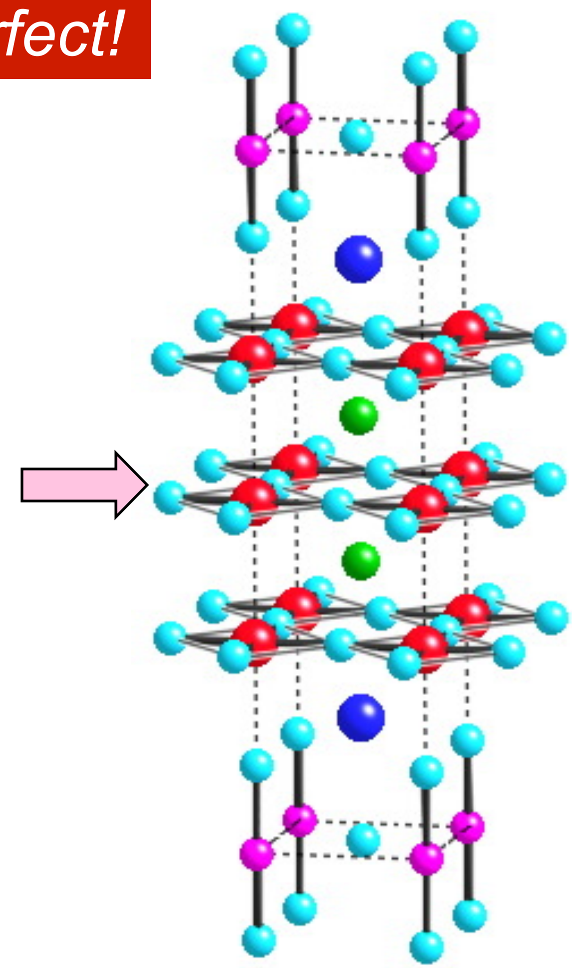


How to raise T_c?

Hg1223 is almost perfect!



Hg1223

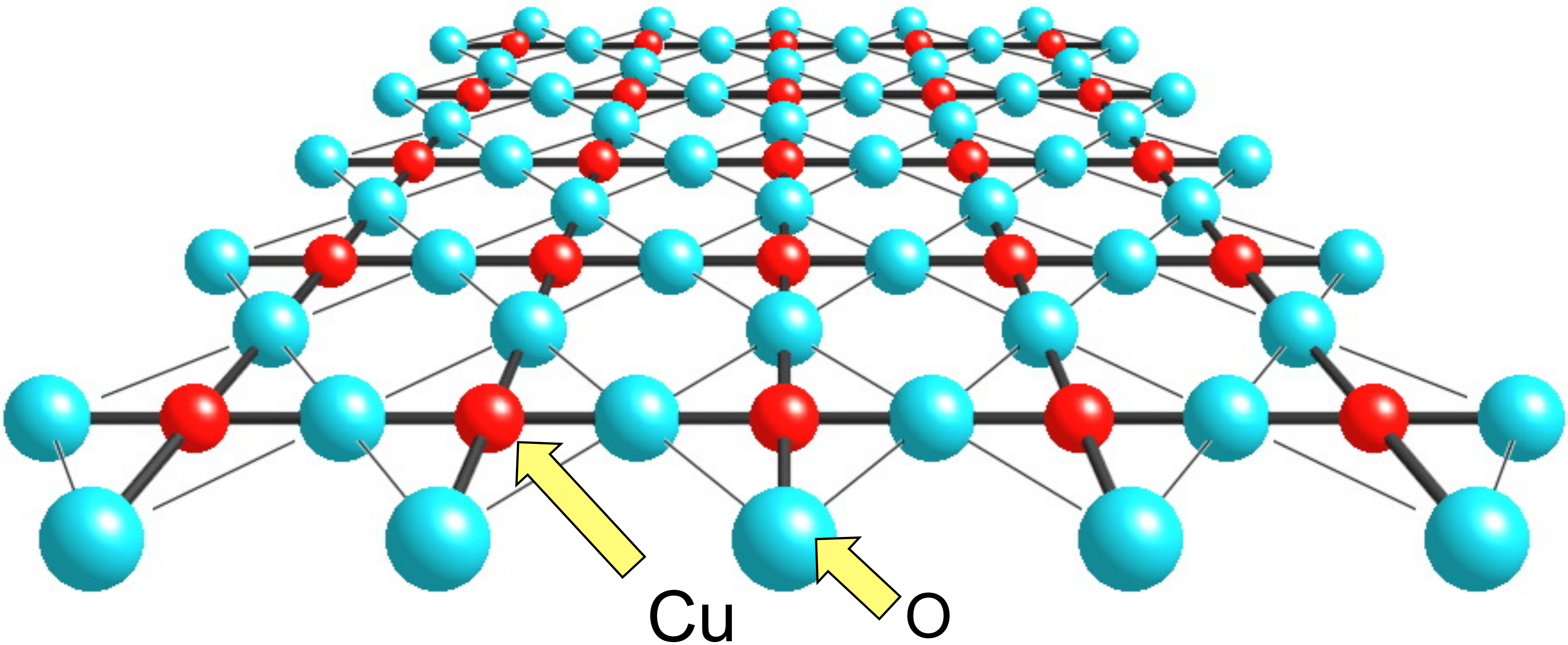


T_c^{max} = 135 K

T_c ~ 160 K at HP

CuO_2 Plane

When holes are introduced into a single CuO_2 plane without any disturbance, ...



Outline

- Introduction to superconductivity
- Copper oxide superconductors:
  Preparation and Materials
- Mechanism of the superconductivity
- What determines the T_c?
- Future prospect

What determines the T_c?

Superconductivity = electron pairs (Cooper pairs)

$$T_c = \underline{\omega} \, \underline{\exp\left(-\frac{1}{\lambda}\right)}$$

An excitation to generate pairing "glue"

damping factor ~ 0.1

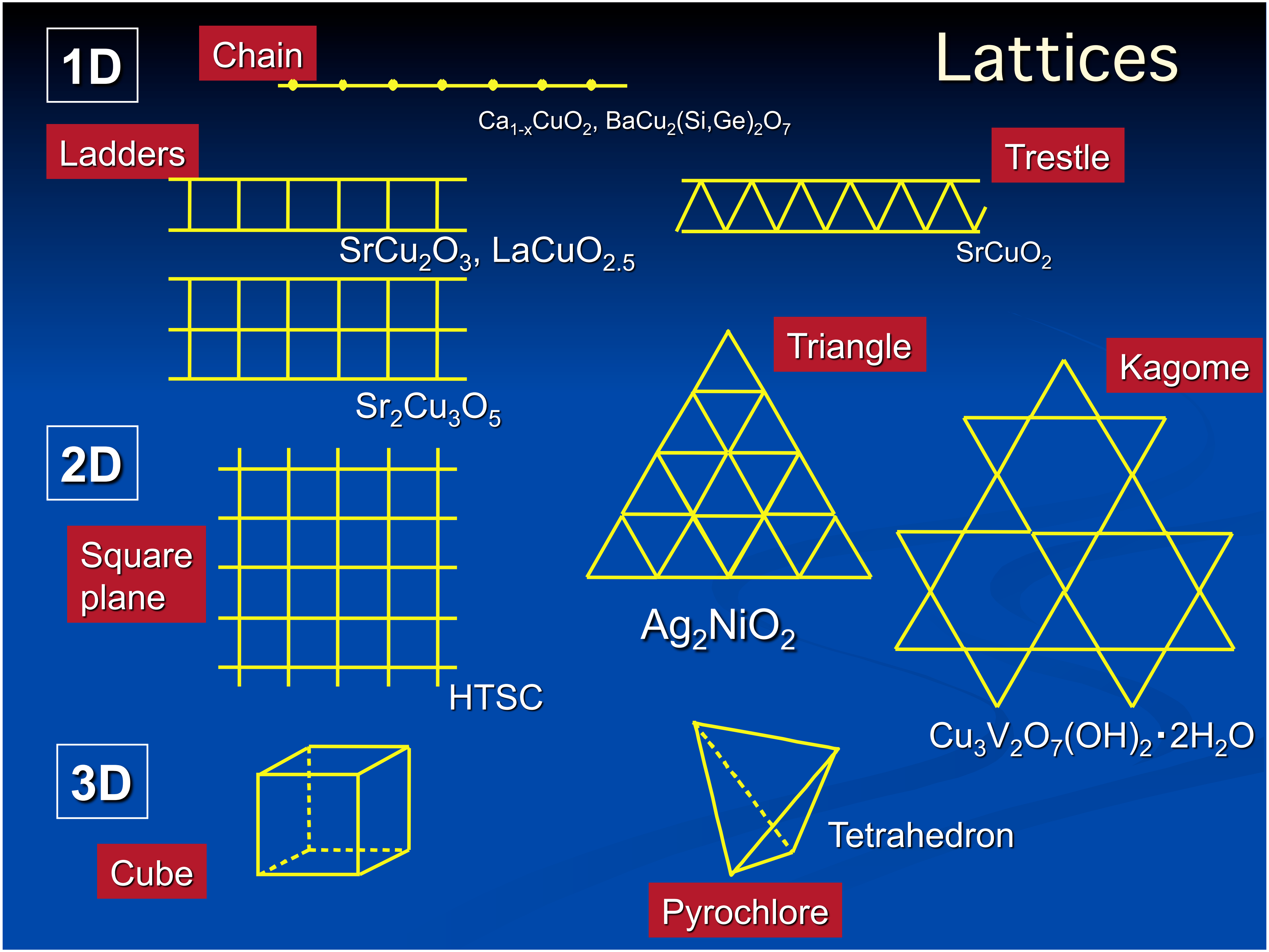
Phonon : $\omega = \omega_{ph}$ ~ 300 K ⇨ T_c ~ 300×0.1 = 30 K

"BCS wall"

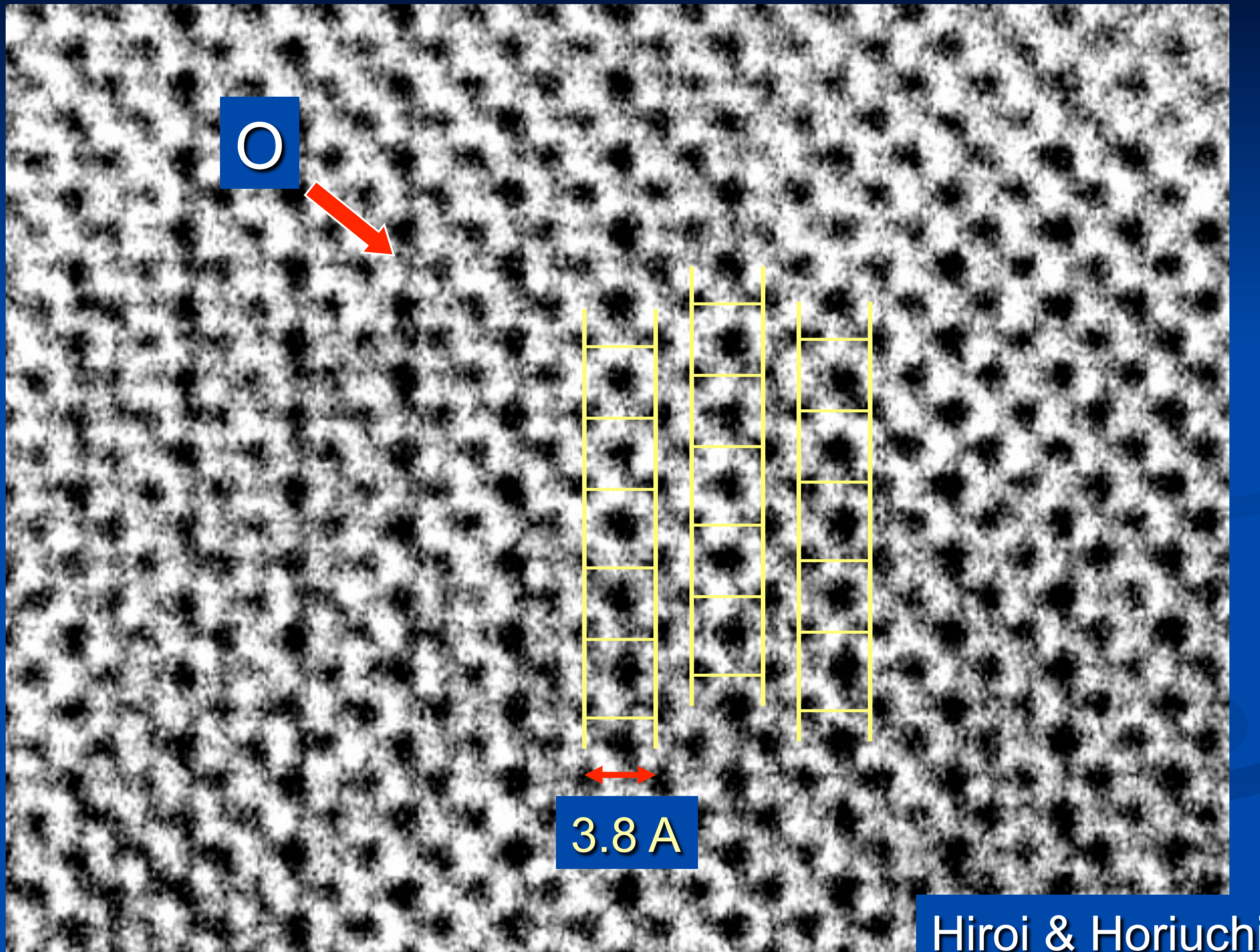
Antiferromagnetic interaction : $\omega = J$ ~ 1500 K ⇨ T_c ~ 1,500×0.1 = 150 K

More glues available for SC?

Let’s find another lattice
to be doped with carriers!

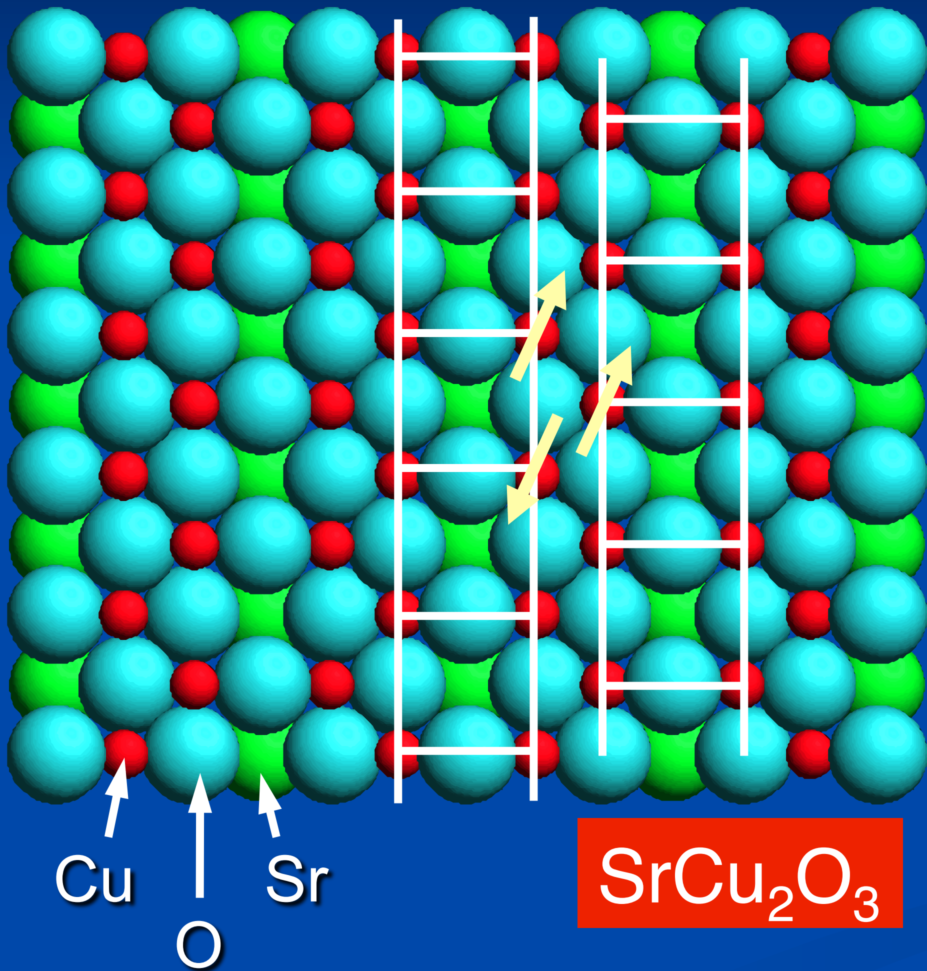

Lattices
1D
Chain
Ca1-xCuO2, BaCu2(Si,Ge)2O7
Ladders
SrCu2O3, LaCuO2.5
Sr2Cu3O5
Trestle
SrCuO2
2D
Square plane
HTSC
Triangle
Ag2NiO2
Kagome
Cu3V2O7(OH)2·2H2O
3D
Cube
Tetrahedron
Pyrochlore

High-resolution electron microscopy



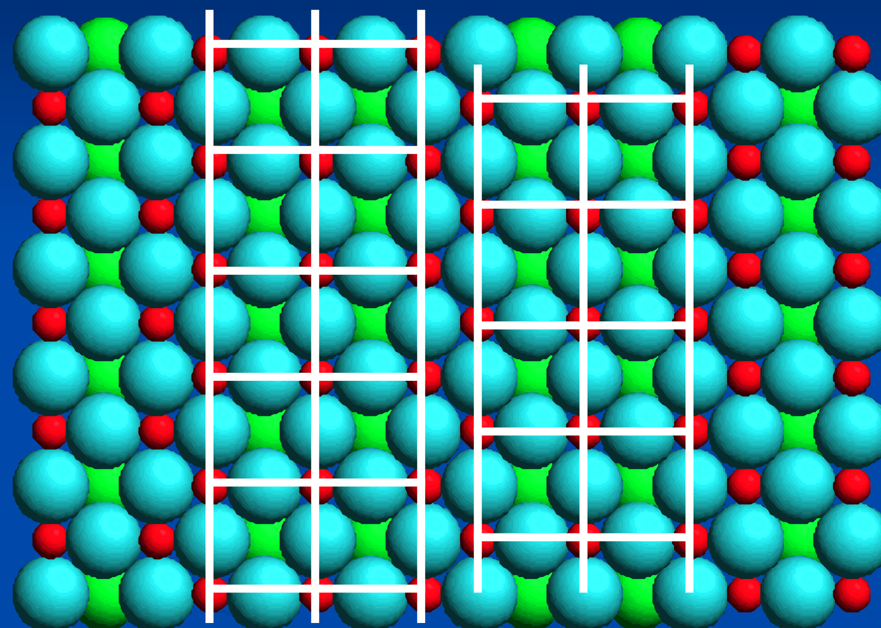
Ladder compounds

two-leg ladder



$SrCu_2O_3$

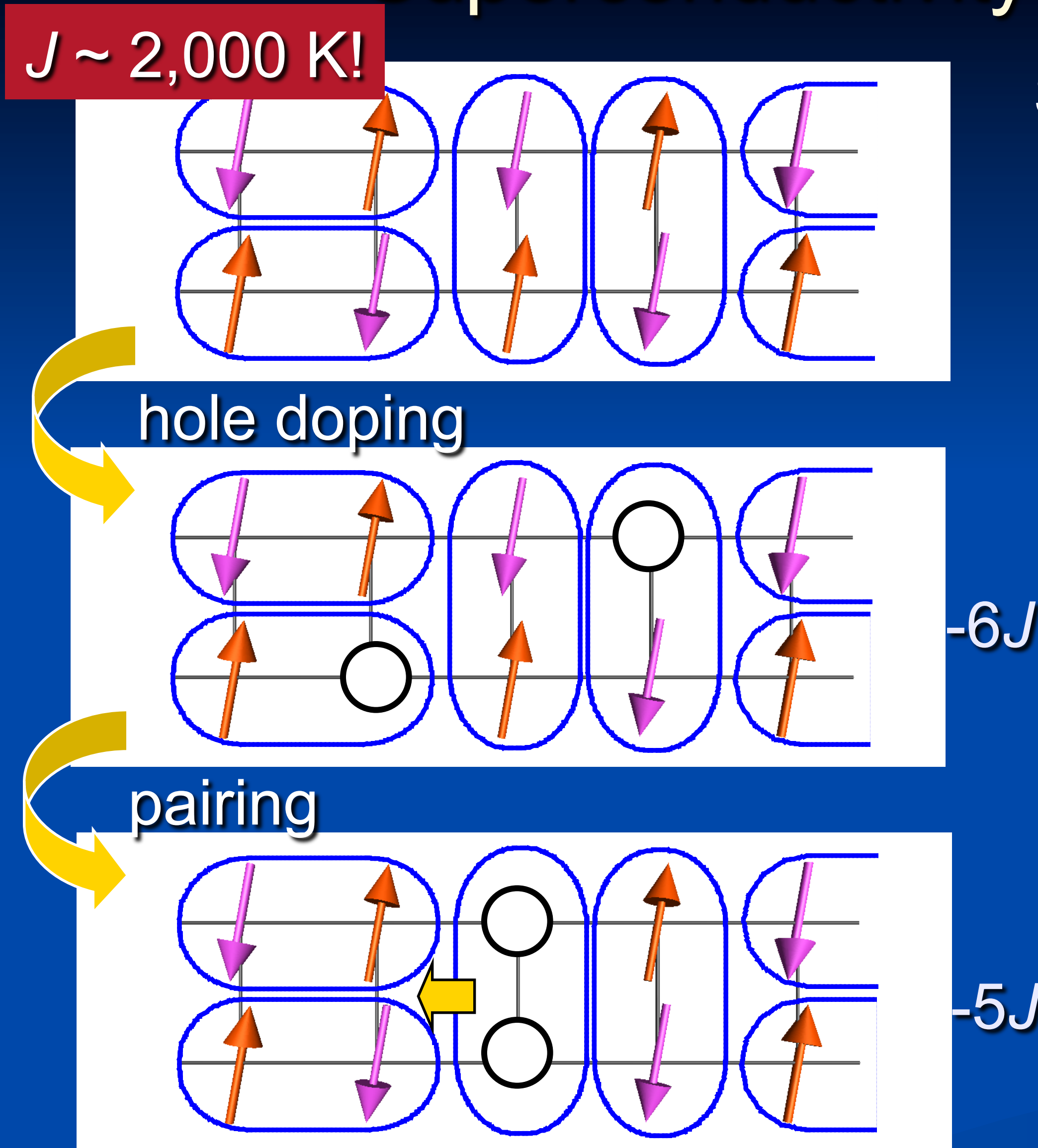
three-leg ladder



$Sr_2Cu_3O_5$

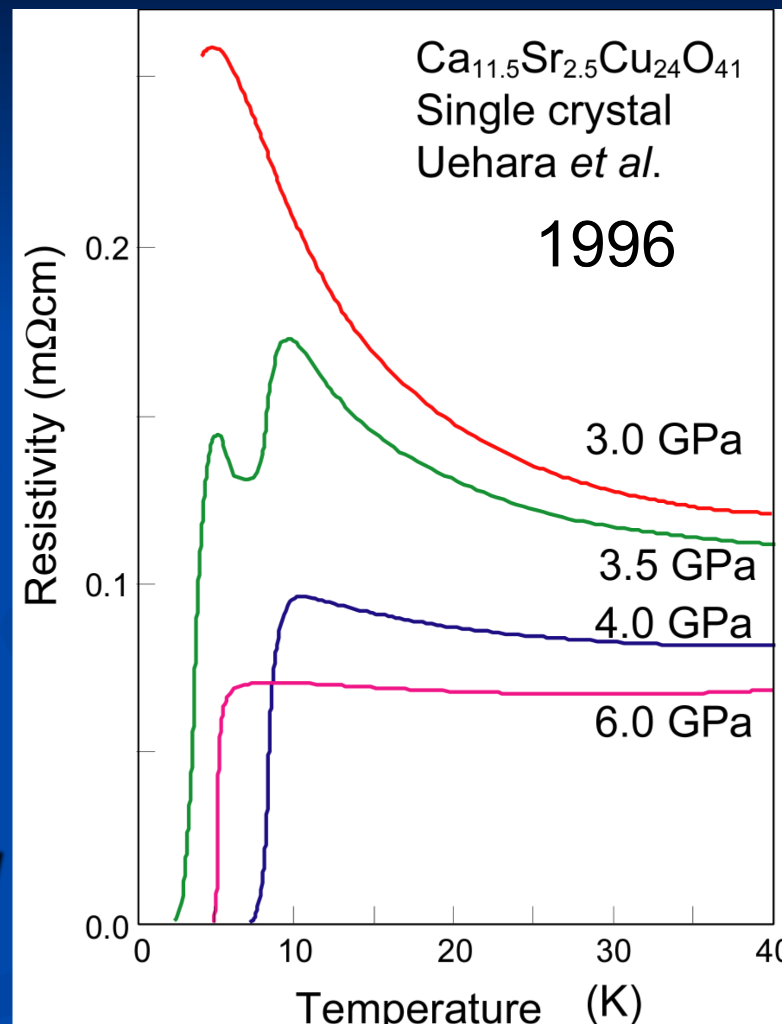
between 1D and 2D

Superconductivity in the two-leg ladder

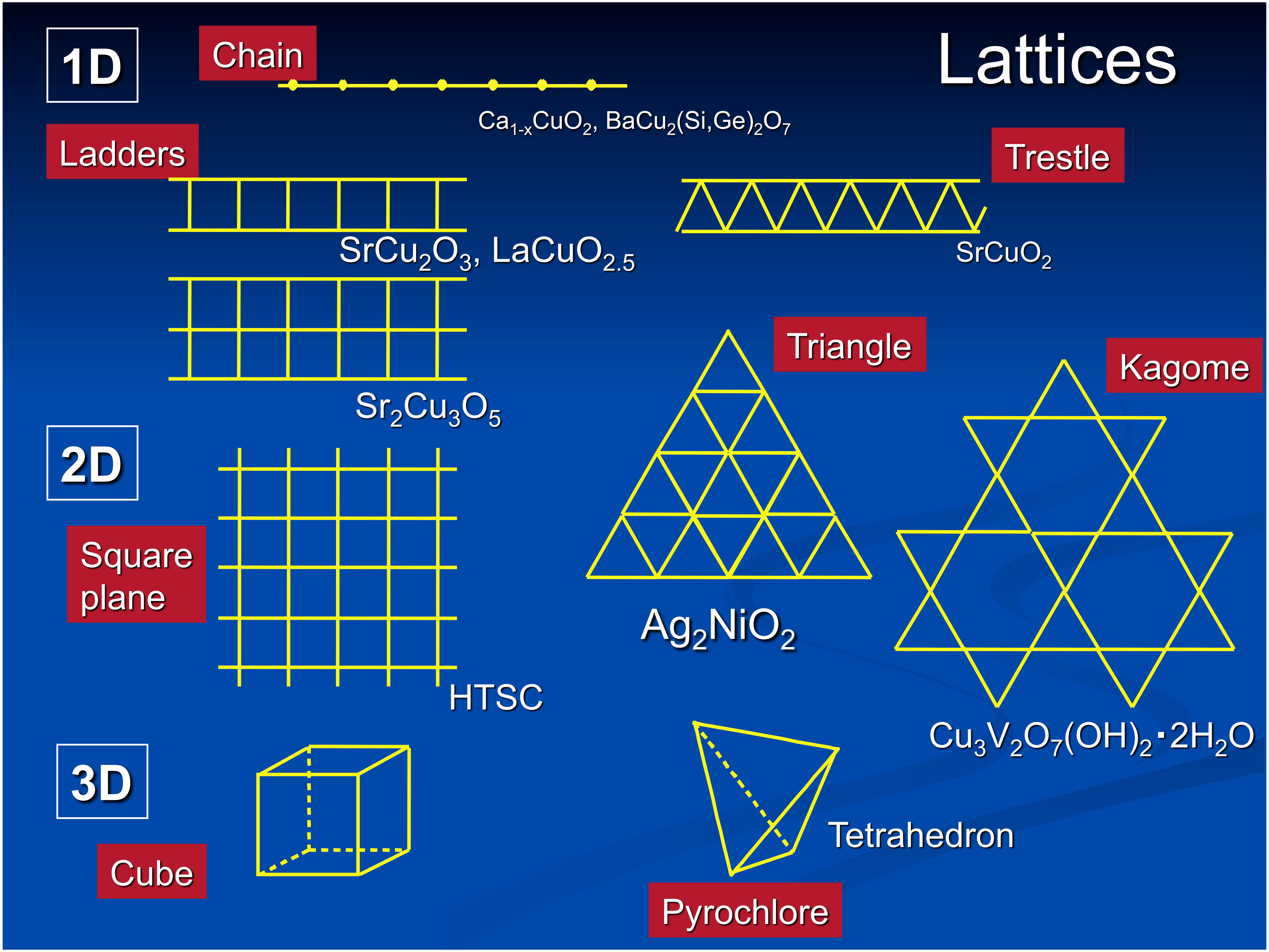


theoretical prediction by E. Dagotto

SC found in $(Ca,Sr)_{14}Cu_{24}O_{41}$



Uehara & Akimitsu

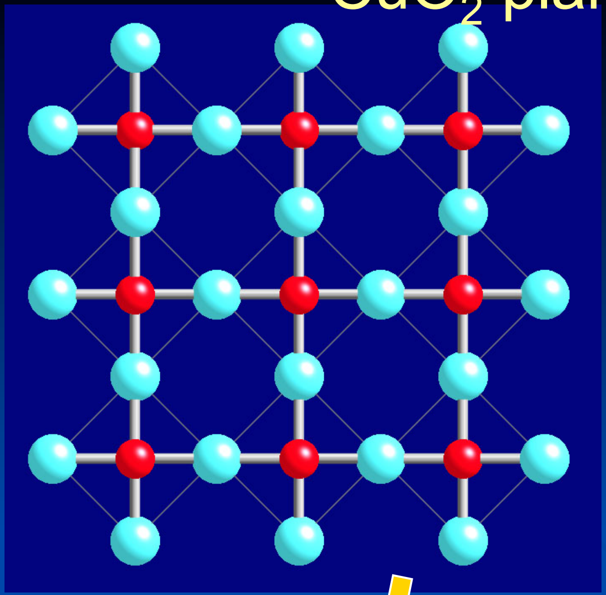


Lattices
1D
Chain
$Ca_{1-x}CuO_2$, $BaCu_2(Si,Ge)_2O_7$
Ladders
$SrCu_2O_3$, $LaCuO_{2.5}$
$Sr_2Cu_3O_5$
Trestle
$SrCuO_2$
2D
Square plane
HTSC
Triangle
Ag_2NiO_2
Kagome
$Cu_3V_2O_7(OH)_2 \cdot 2H_2O$
3D
Cube
Tetrahedron
Pyrochlore

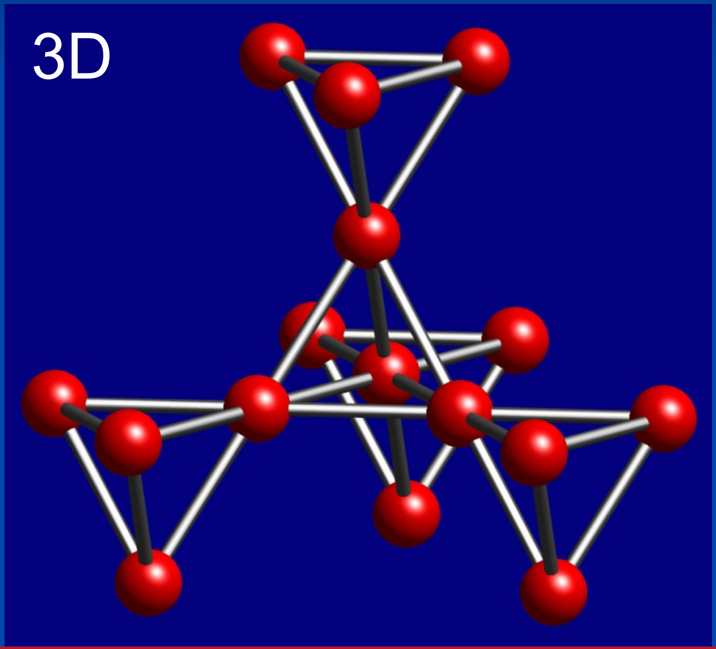
Squares to triangles

More interesting Superconductors?

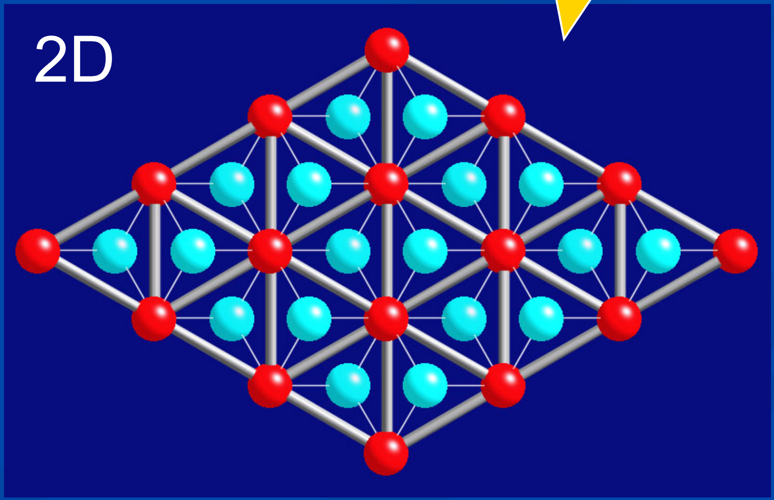
CuO$_2$ plane



pyrochlore lattice



α-pyrochlore $Cd_2Re_2O_7$
β-pyrochlore AOs_2O_6



$Na_xCoO_2 \cdot yH_2O$ (Takada)

Toward a higher T_c

1. Increase ω!

Fundamental interaction	Energy scale	Maximum T_c
phonons	$\omega \lesssim 300$ K	30 K
spins	$\omega = J$	
2D AF	$J \sim 1500$ K	150 K
1D AF	$J \lesssim 3000$ K	×
FM	$J_{FM} << J_{AF}$	

Exitons (1D or interface)
Charge fluctuations, ...

$$T_c = \omega \exp\left(-\frac{1}{VN(E_F)}\right)$$

$T_c \rightarrow \omega$, as $VN(E_F)\uparrow$

2. Increase V!

but, $V\uparrow$; $\omega\downarrow$ in phonons.

3. Suppress competing order!

dimensionality: 3D > 2D <1D
frustration
carrier doping

Iron Age？

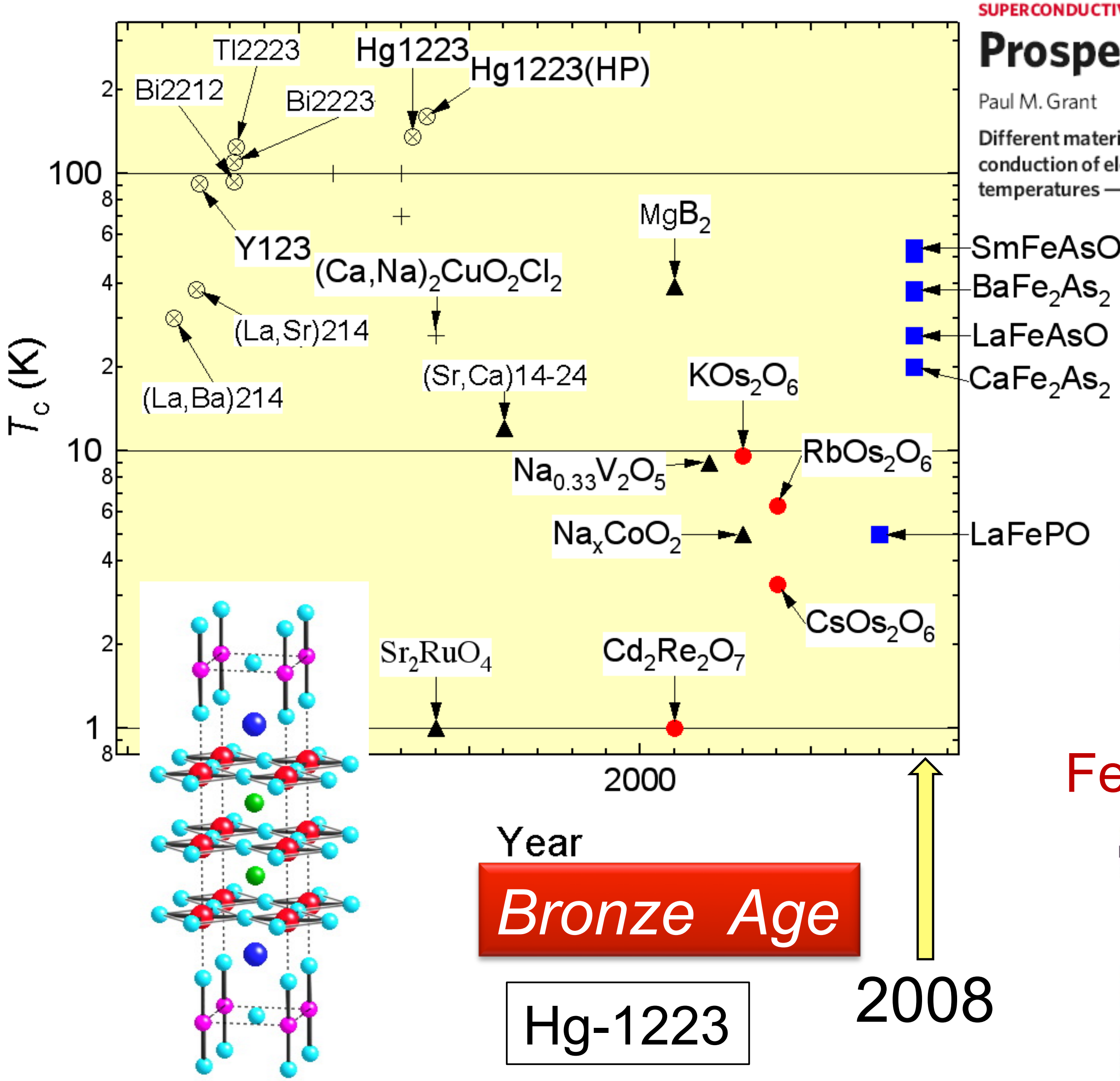
Iron Age

SUPERCONDUCTIVITY

Prospecting for an iron age

Paul M. Grant

Different material options for high-temperature superconductivity — conduction of electricity with little or no resistance at 'practical' temperatures — have arrived. Iron compounds are the latest thing.



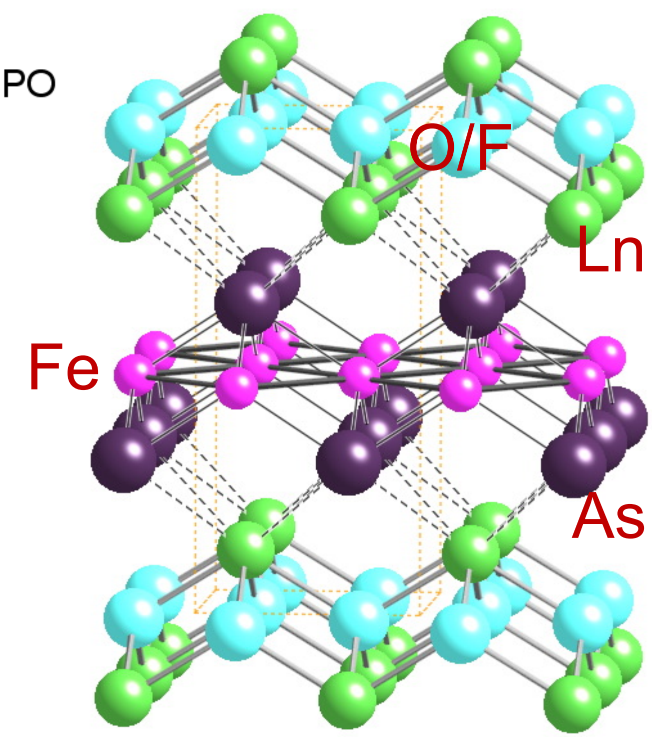
Bronze Age

Hg-1223

2008

LnFeAsO

T_c = 54 K



Crazy paper from ...

Superconductivity in $FeTe_{1-x}S_x$ induced by alcohol

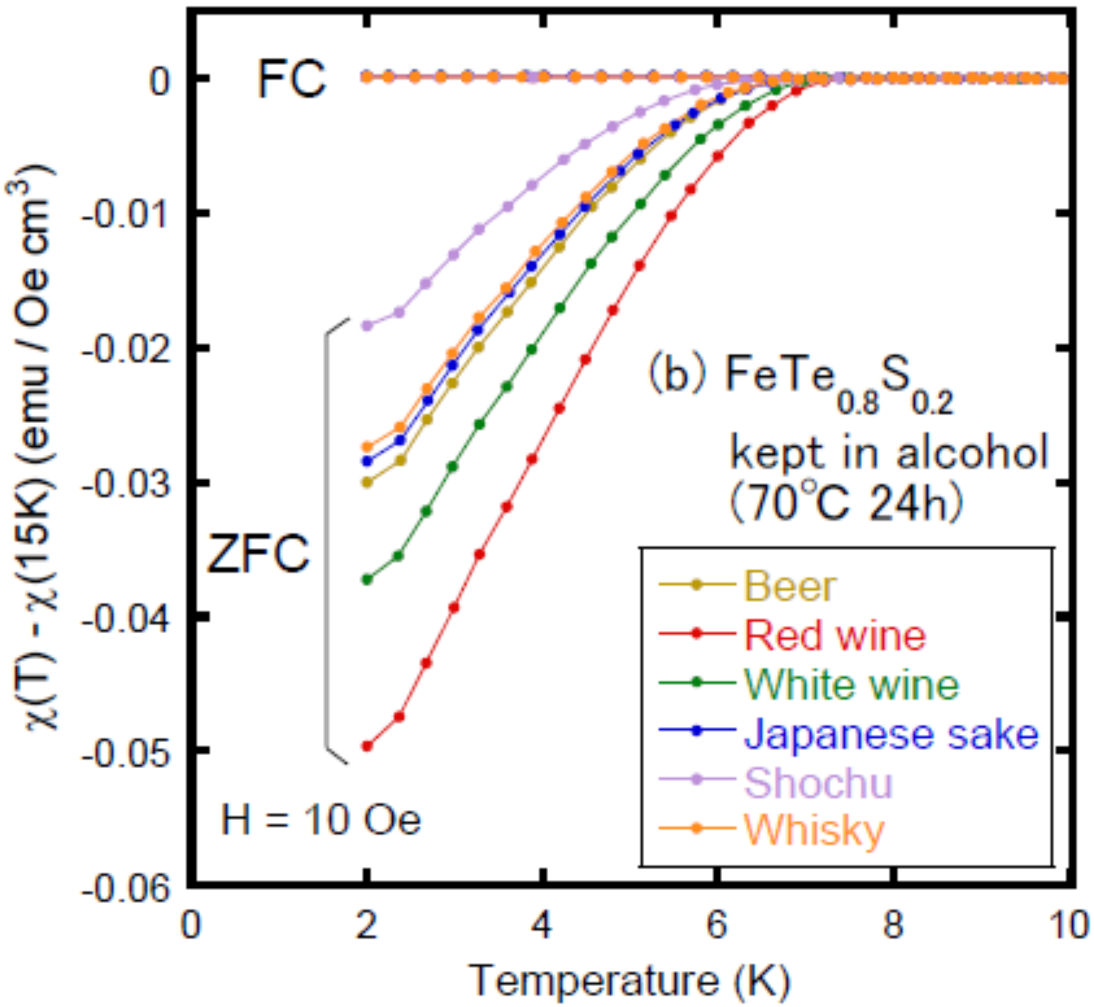
Keita Deguchi[1,2,3], Yoshikazu Mizuguchi[1,2,3], Toshinori Ozaki[1,3], Shunsuke Tsuda[1,3], Takahide Yamaguchi[1,3] and Yoshihiko Takano[1,2,3]

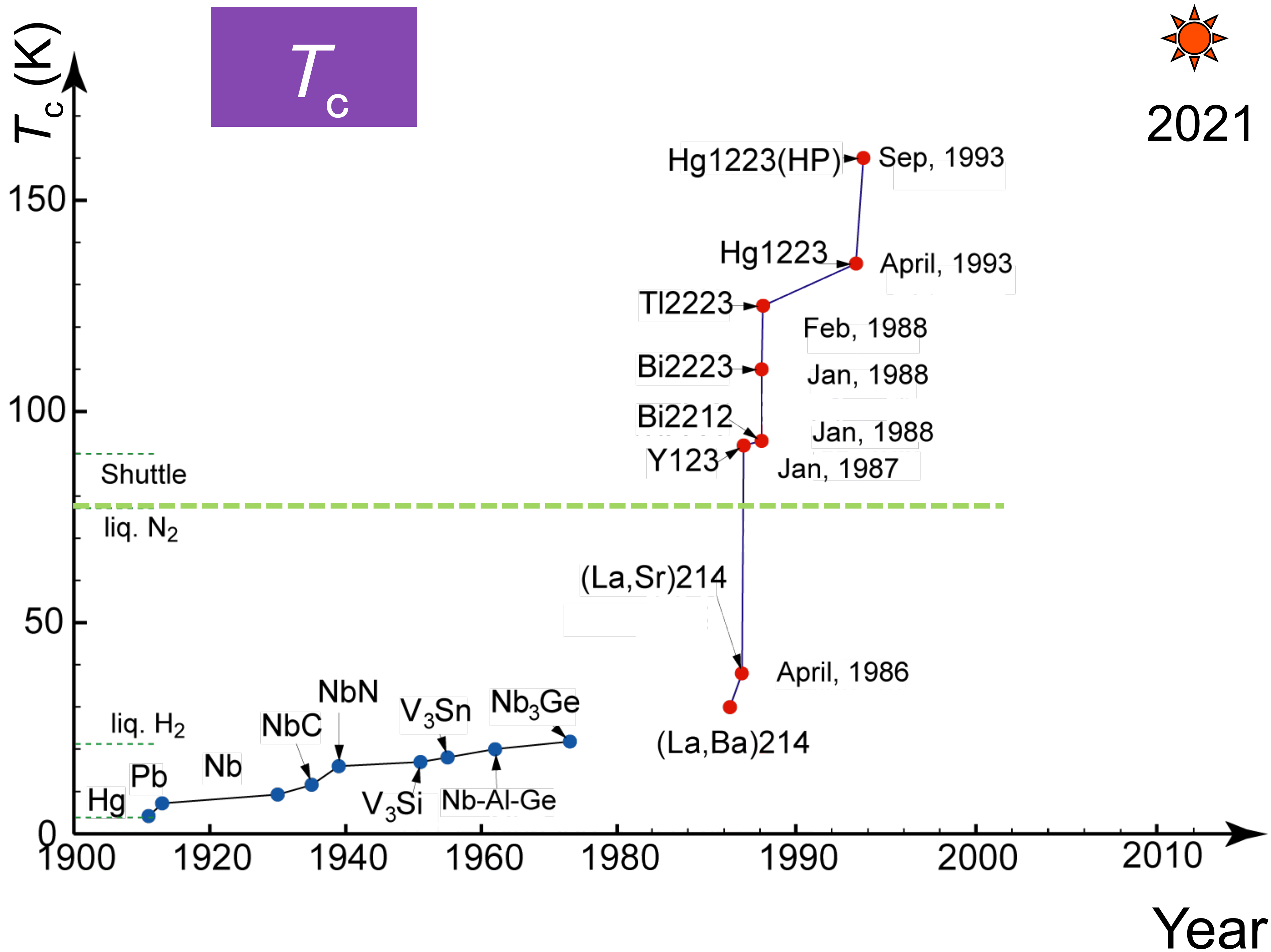
1. National Institute for Materials Science, 1-2-1

2. University of Tsukuba, 1-1-1 Tennodai, Tsukul

3. JST-TRIP, 1-2-1, Sengen, Tsukuba, 305-0047, .

may be suitable for Nature or Science, but not for Journals!





T_c
2021
T_c (K)
150
100
50
0
Shuttle
liq. N_2
liq. H_2
Hg
Pb
Nb
NbC
NbN
V_3Si
V_3Sn
Nb-Al-Ge
Nb_3Ge
(La,Ba)214
(La,Sr)214
April, 1986
Y123
Jan, 1987
Bi2212
Jan, 1988
Bi2223
Jan, 1988
Tl2223
Feb, 1988
Hg1223
April, 1993
Hg1223(HP)
Sep, 1993
1900
1920
1940
1960
1980
1990
2000
2010
Year

Applications of SC

Future

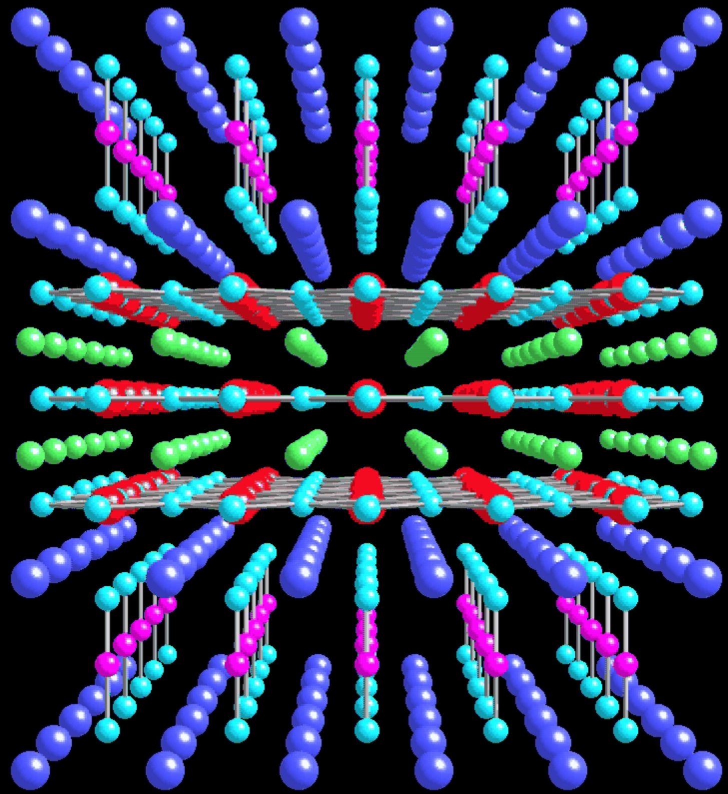
If there is a room-temperature superconductor,
unnecessary for cooling,
already $\rho = 0$ in a chilly morning,
and have to warm it to measure the transition.

Is it good for applications?

New materials science?

Interesting physics behind?

Nobel prize?



Where is a room-temperature superconductor？

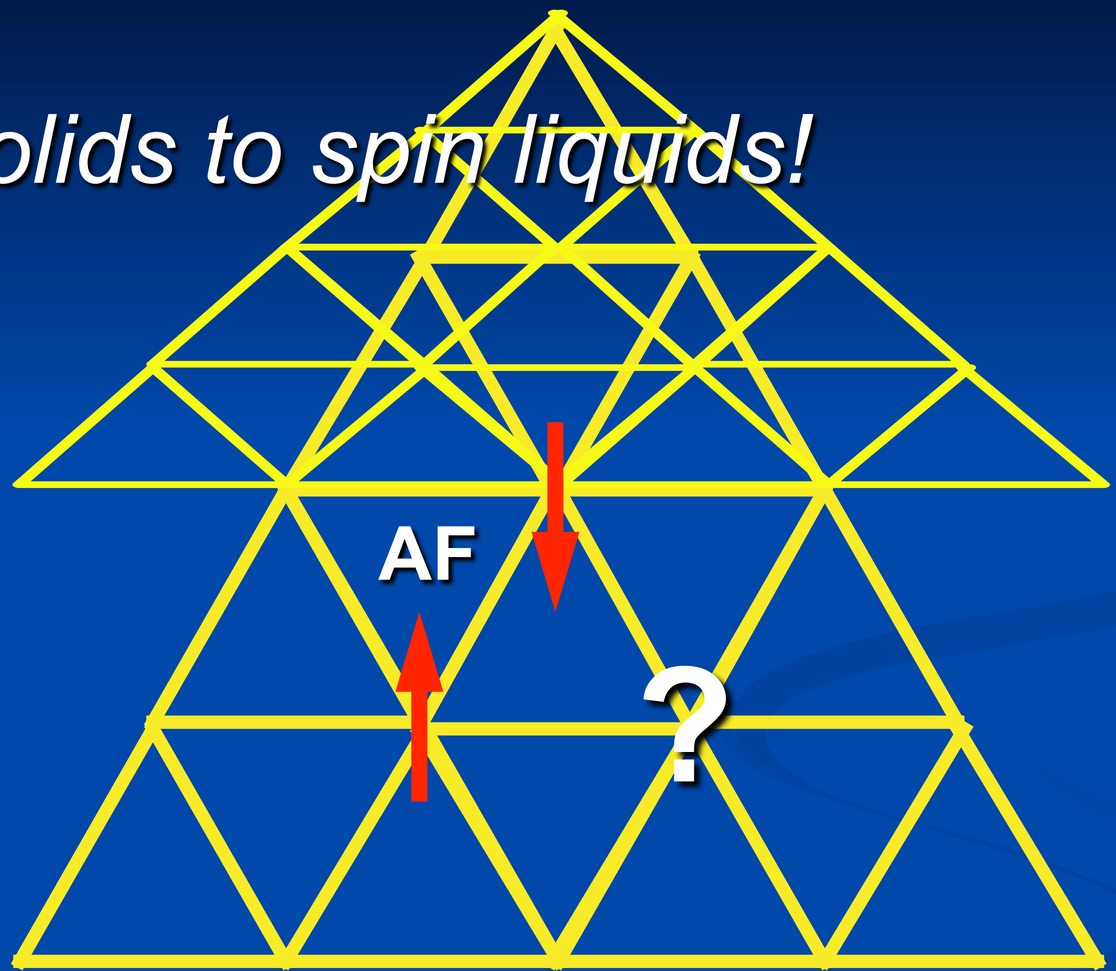
Hg1223

Those who have been working on the copper oxides for many years may not be able to find it.

For young people, just forget my story and try!

Geometrical Frustration

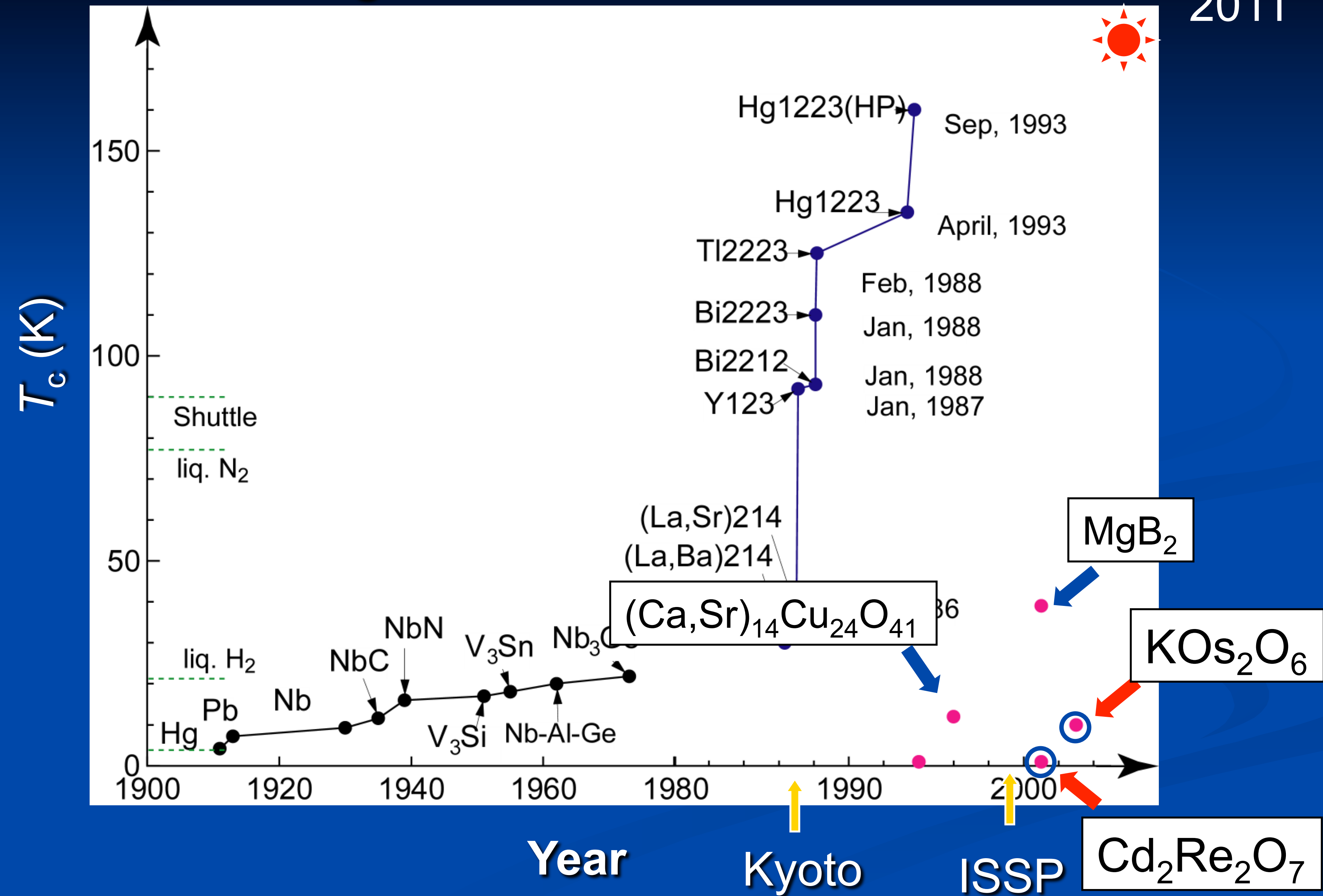
Spin solids to spin liquids!



What would happen when it is doped with carriers?

High-T_c superconductors

2011



モット絶縁体
vs
スピンゆらぎ

守谷 亨
磁性物理学
朝倉書店2006

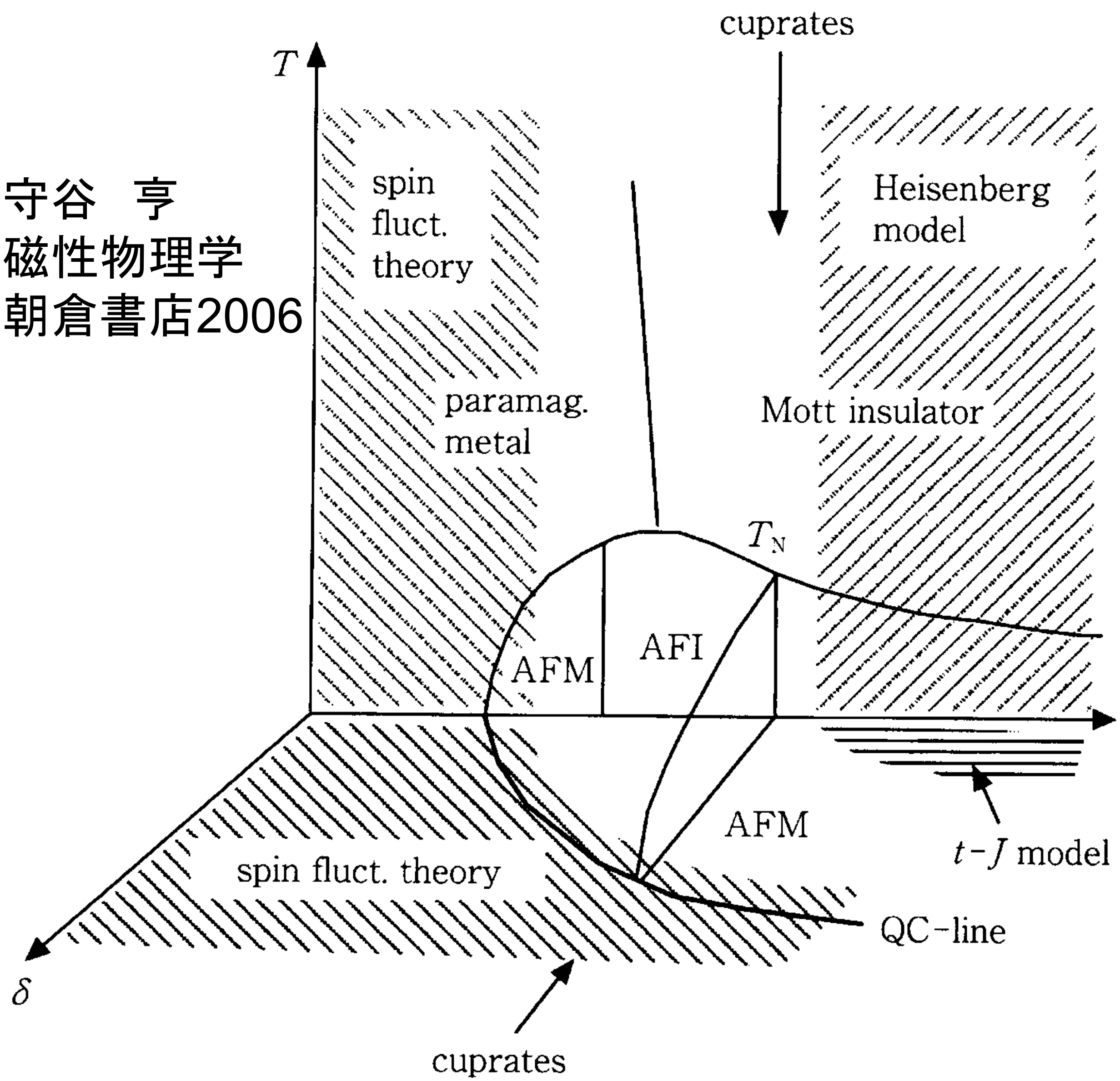
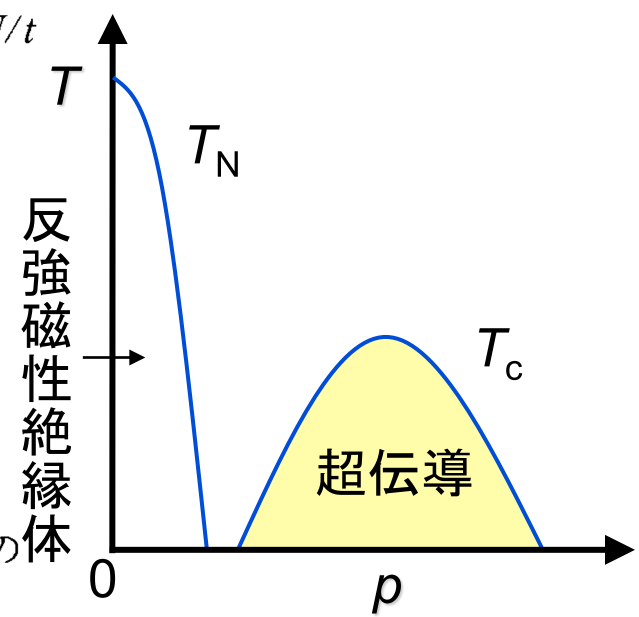


図 9.10 擬 2 次元ないし 3 次元ハバード・モデルの相図
超伝導ペアリングの可能性は未だ考慮されていない．T 軸に垂直な面内の陰影部分は T 軸に沿って上に伸ばした空間領域を意味する．

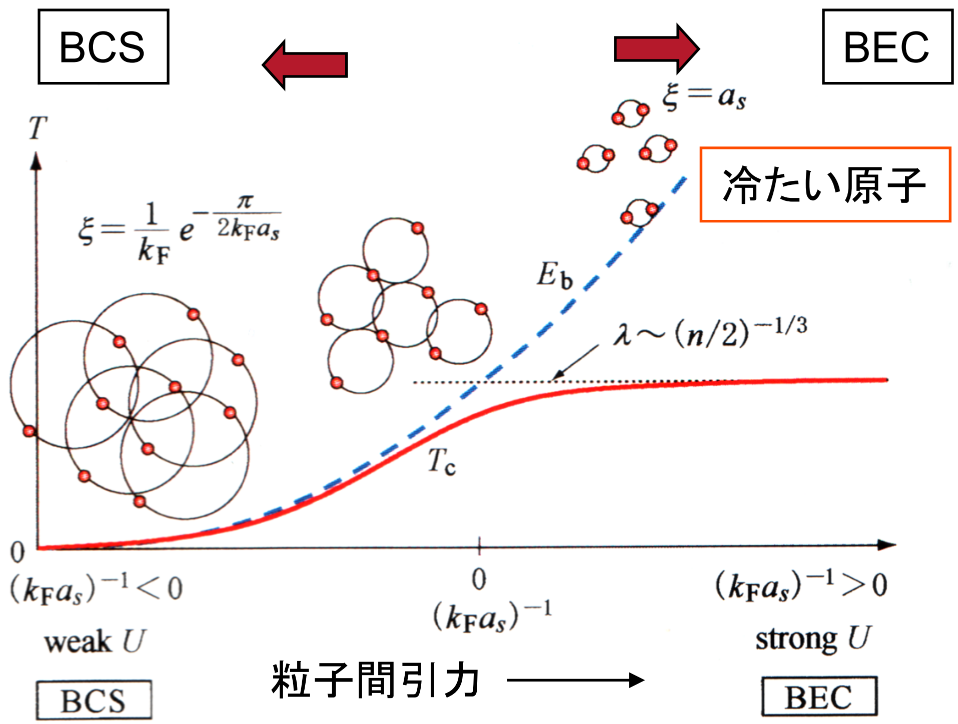


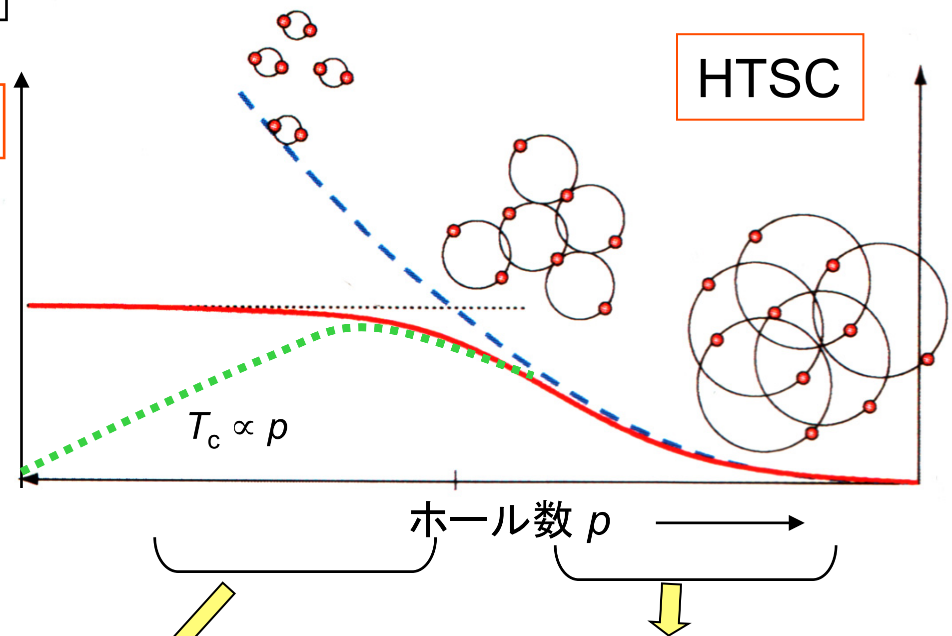
BCS-BEC Crossover

高温超伝導との類似性

クーパー対形成に
よるBCS超伝導

分子ボゾンのボーズーア
インシュタイン凝縮





$$k_B T_c = \left(2\pi\hbar^2/m\right)\left(n/2.612\right)^{2/3}$$

$$n \bullet \lambda_{th}^3 = 2.612$$

クーパー対形成に
フェルミ面は不要！

強結合
反強磁性バックグラウンドによる
　強い引力
フォノンなどの「のり」はない
小さなクーパーペア
T_c以上でクーパーペアは出来る
　が波動関数は重ならない
T_cでBEC，つまり，超伝導
T_cは密度に比例（2D）

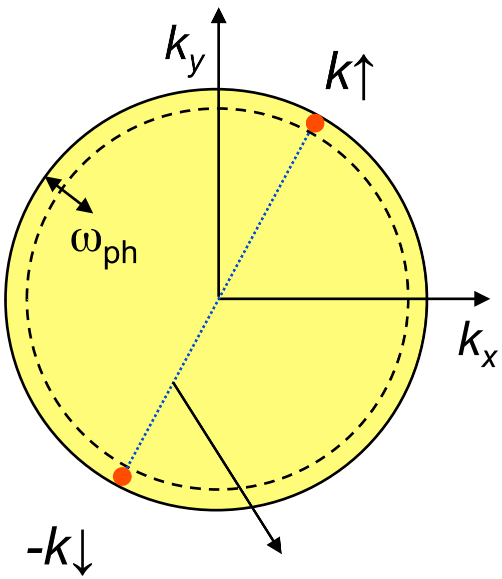
弱結合
引力低下と共にT_cは下がる
大きなクーパーペア
T_cでペアが出来ると同時に
　波動関数は重なる
クーパー対形成と超伝導
　転移は同時に起こる
弱結合BCS領域
T_cは相互作用の大きさによる

Basic idea of the BCS-type superconductivity

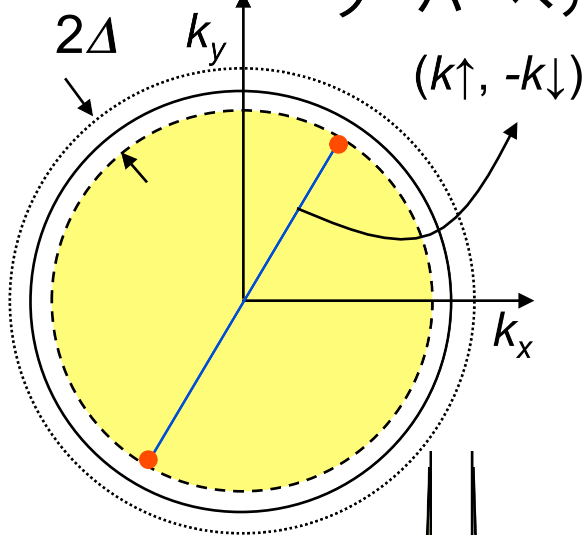
常伝導状態

超伝導状態

電子：フェルミオン



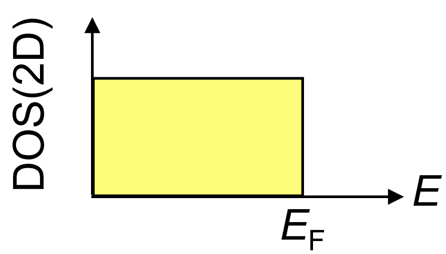
クーパーペア：ボソン

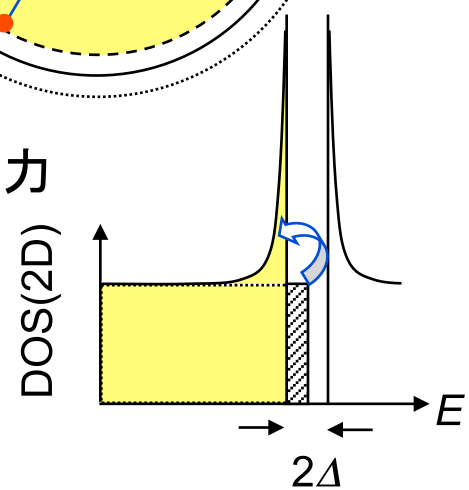


フェルミ面近傍（ω_{ph}程度のエネルギー幅）の電子間にフォノンを媒介とした引力が働くと，クーパーペアが形成されてエネルギーギャップが生じる．

わずかでも電子ー格子相互作用があれば，フェルミ面は不安定となり，超伝導状態に転移する

フォノンを媒介とする引力





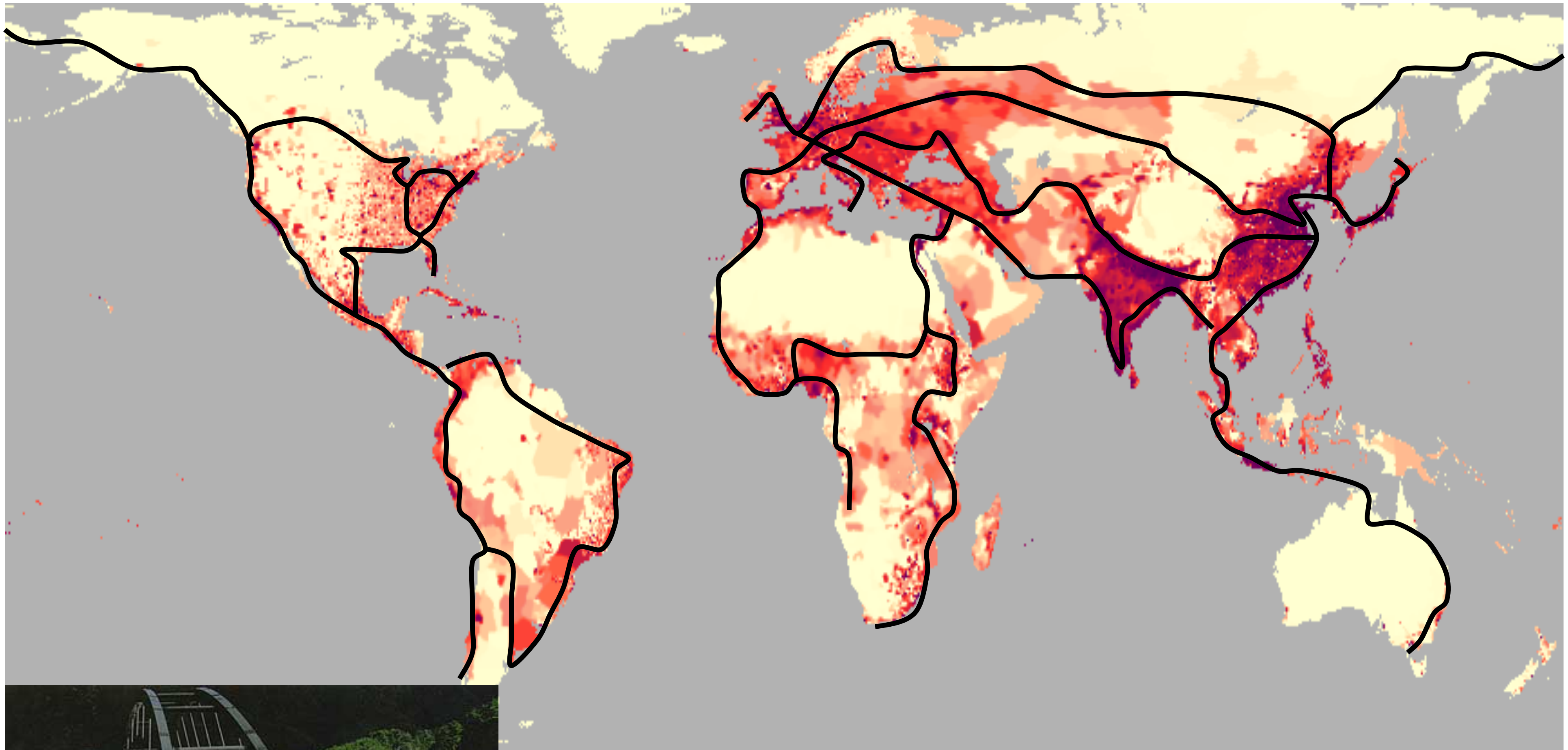
T = 0 K
フェルミ縮退

$2\Delta = 3.5k_BT_c$

弱結合BCS状態
k空間におけるペアリング

$$T_c = \omega_{ph}\exp\left(-\frac{1}{VN(E_F)}\right)$$

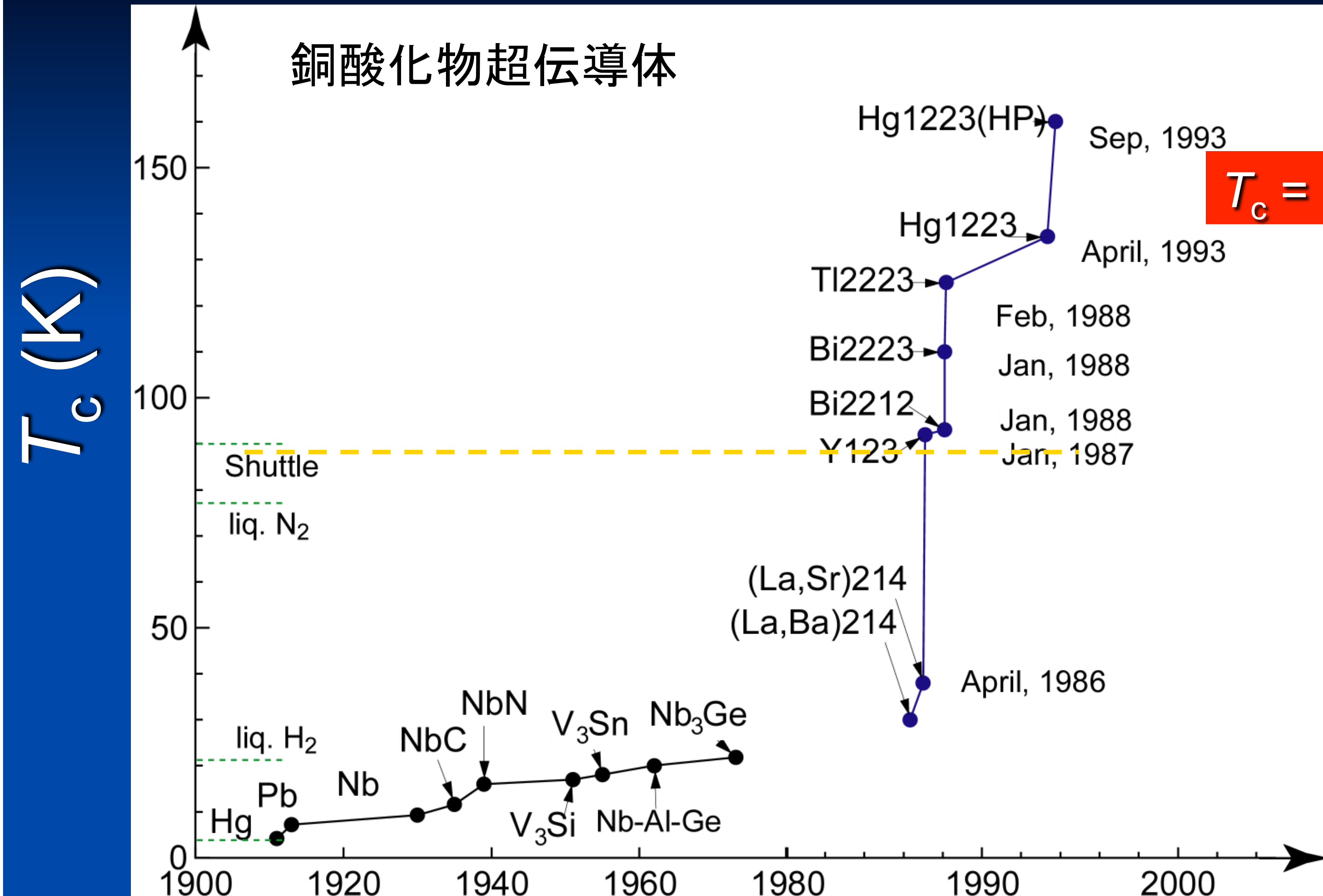
人口密度分布とリニア路線



PROPOSED MAGLEV PATHS

K.Kitazawa: Moscow Int. Conf. MSU 2001

High Temperature Superconductors



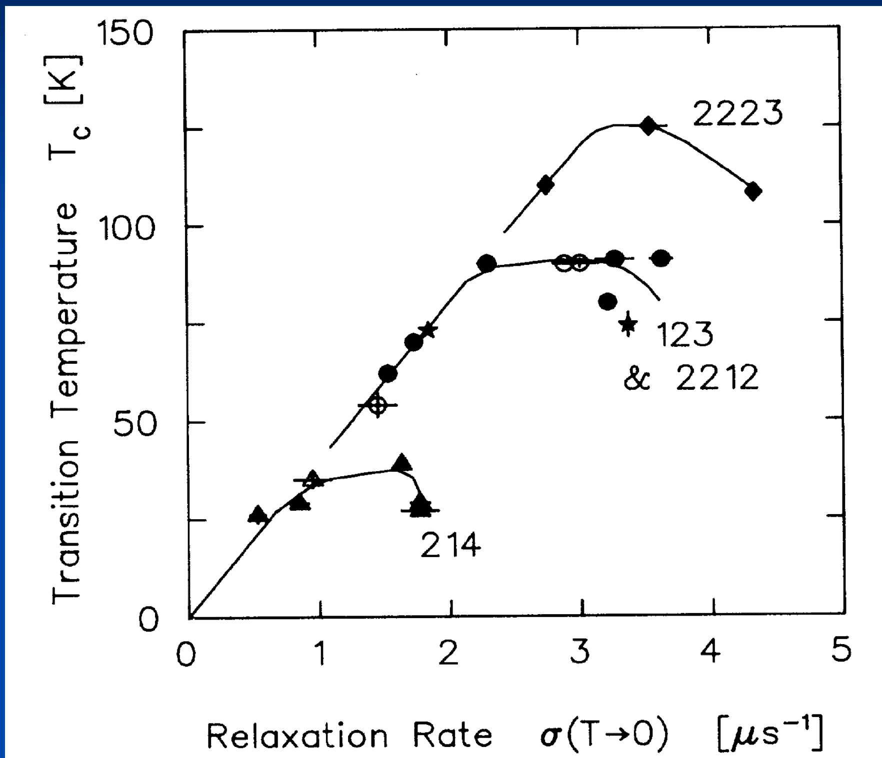
T_c = 135 K

Kyoto

ISSP

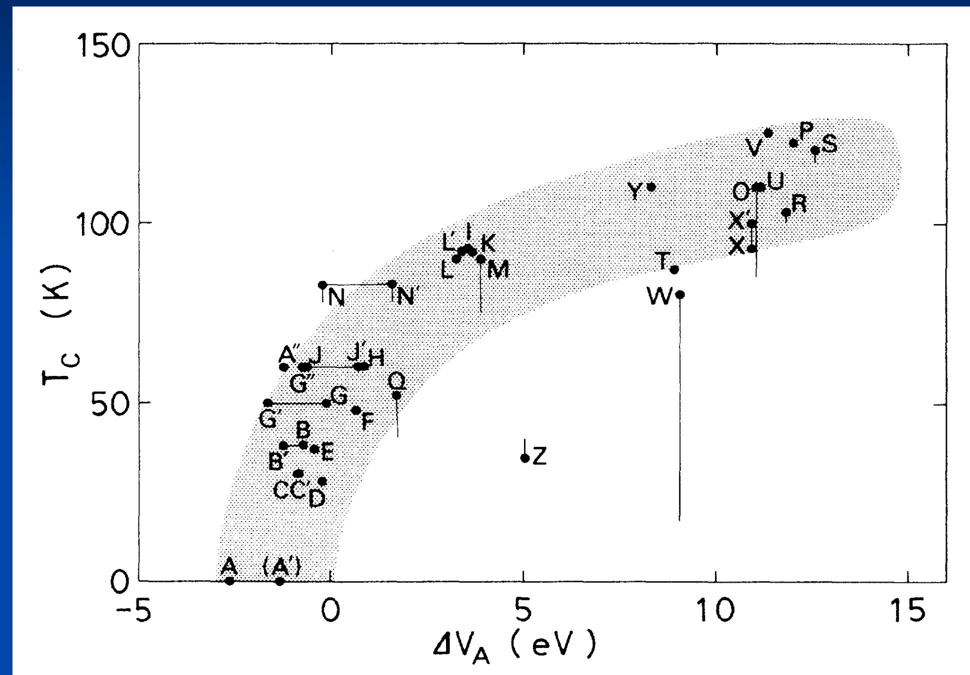
Uemura plot & Maekawa plot

T_c vs n_s/m^*



Y. J. Uemura, *et al.*, PRL 62, 2317 (1989).

T_c vs ΔV_A

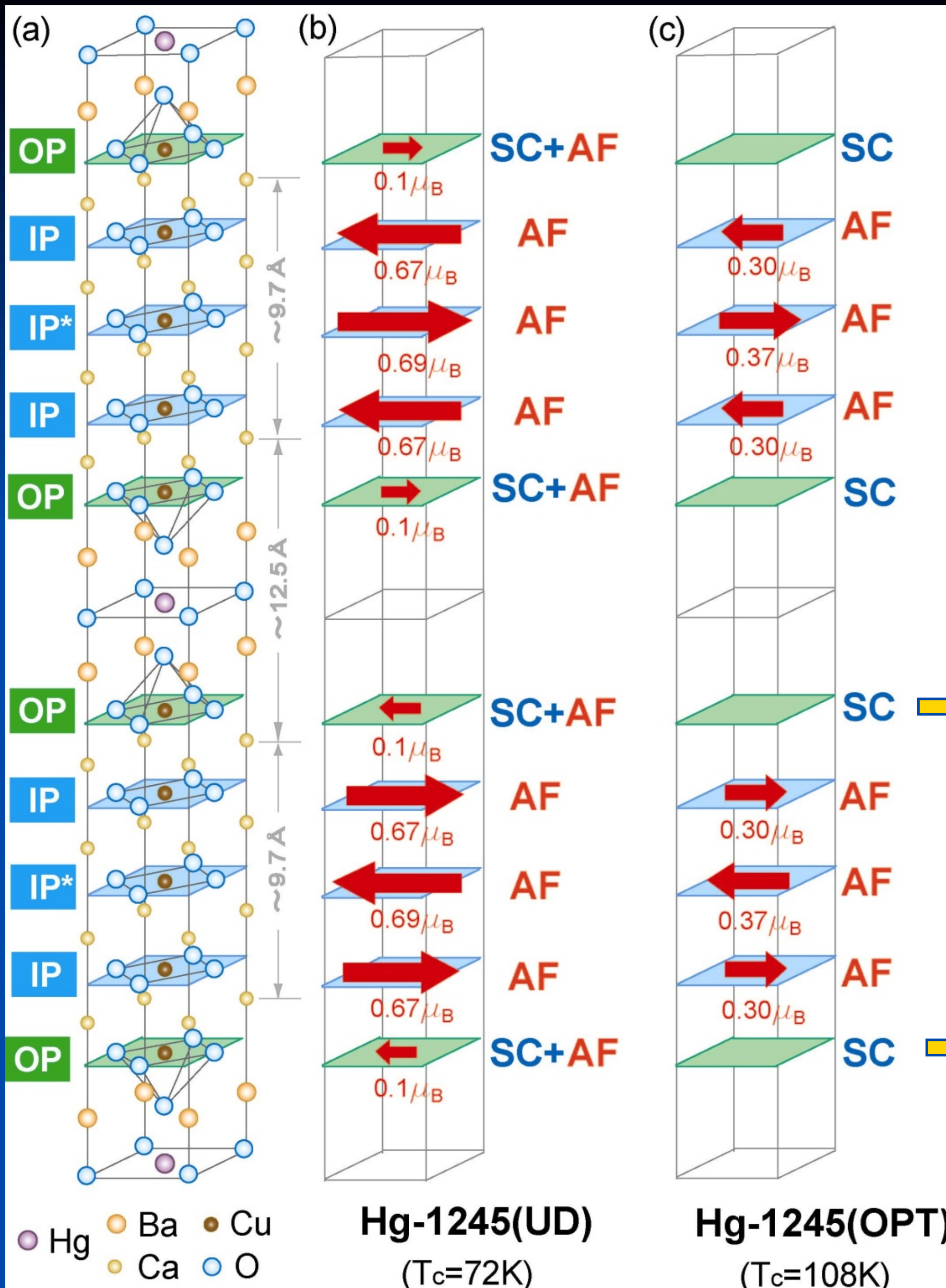


$$\Delta V_A = V_{O(A)} - V_{O(P)}$$

Y. Ohta, T. Toyama & S. Maekawa, PRB 43, 2968 (1991).

Multilayered Superconductors

Hg1245 with 5 CuO_2 planes



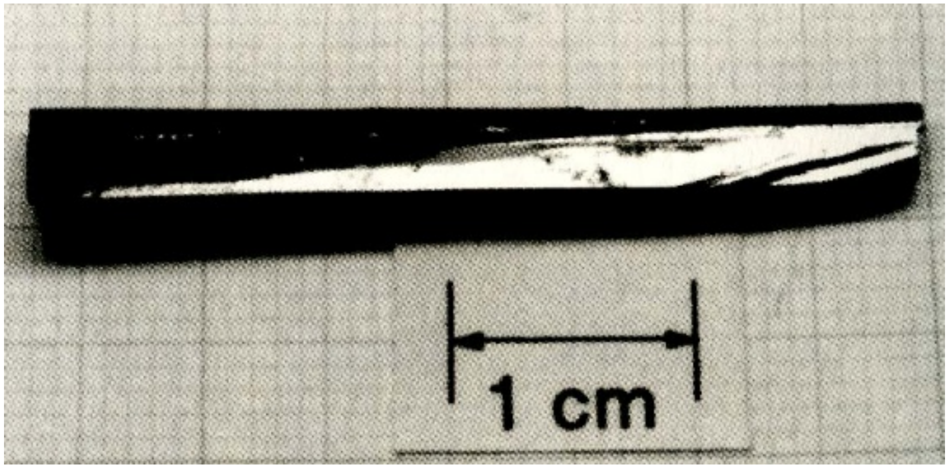
T_c = 108 K

AF with less holes

T_c = 108 K

H. Mukuda, *et al*., PRL 96, 087001 (2006).

Bi HTSCs



Large single crystals