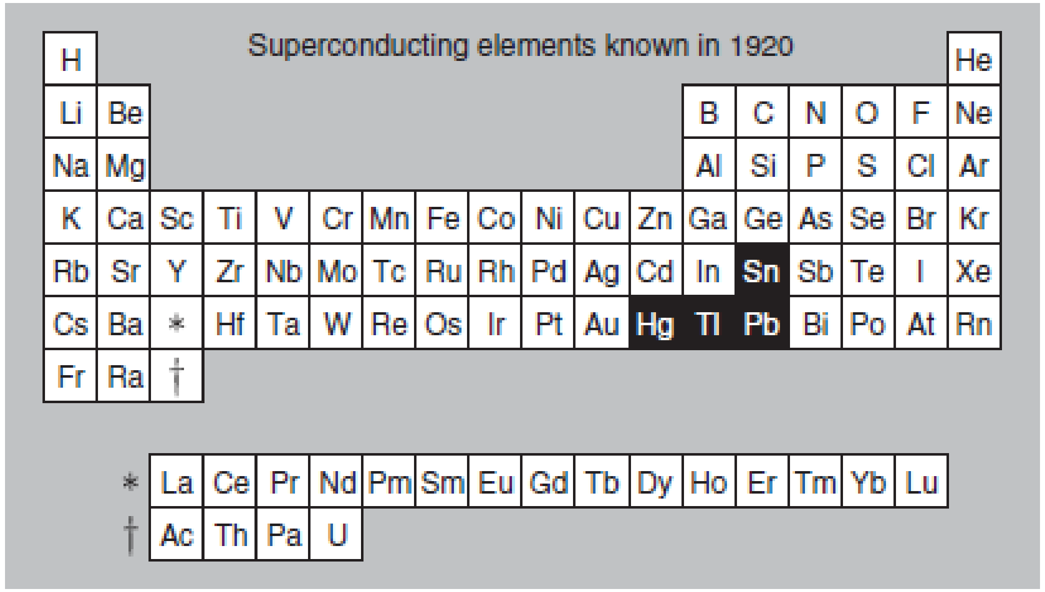
Superconductive Materials

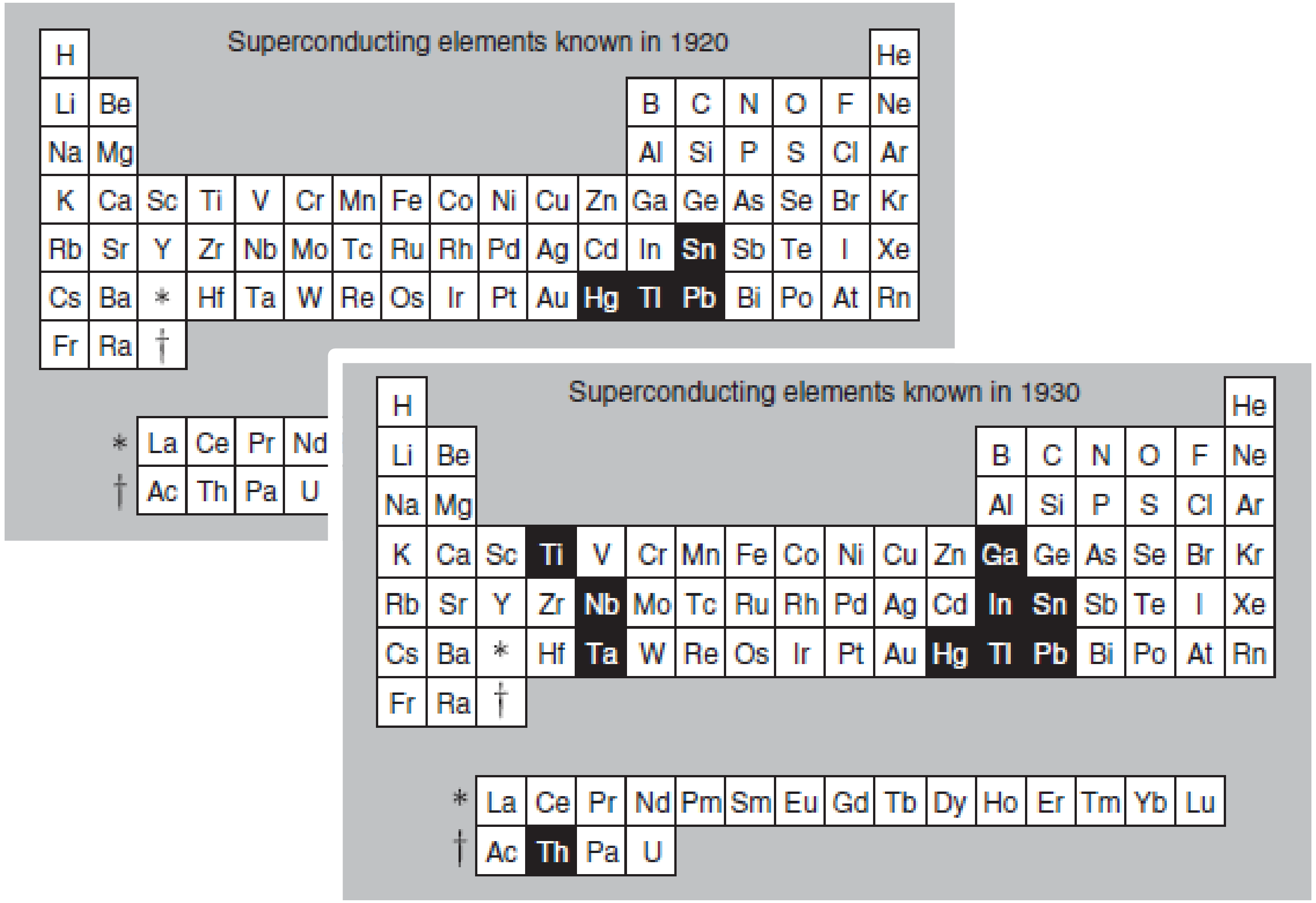
Part 8

Superconductive Materials: elements, alloys and HTS

Superconducting elements


Superconducting elements known in 1920

Superconducting elements



Superconducting elements known in 1920

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	**Sn**	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	**Hg**	**Tl**	**Pb**	Bi	Po	At	Rn
Fr	Ra	†															

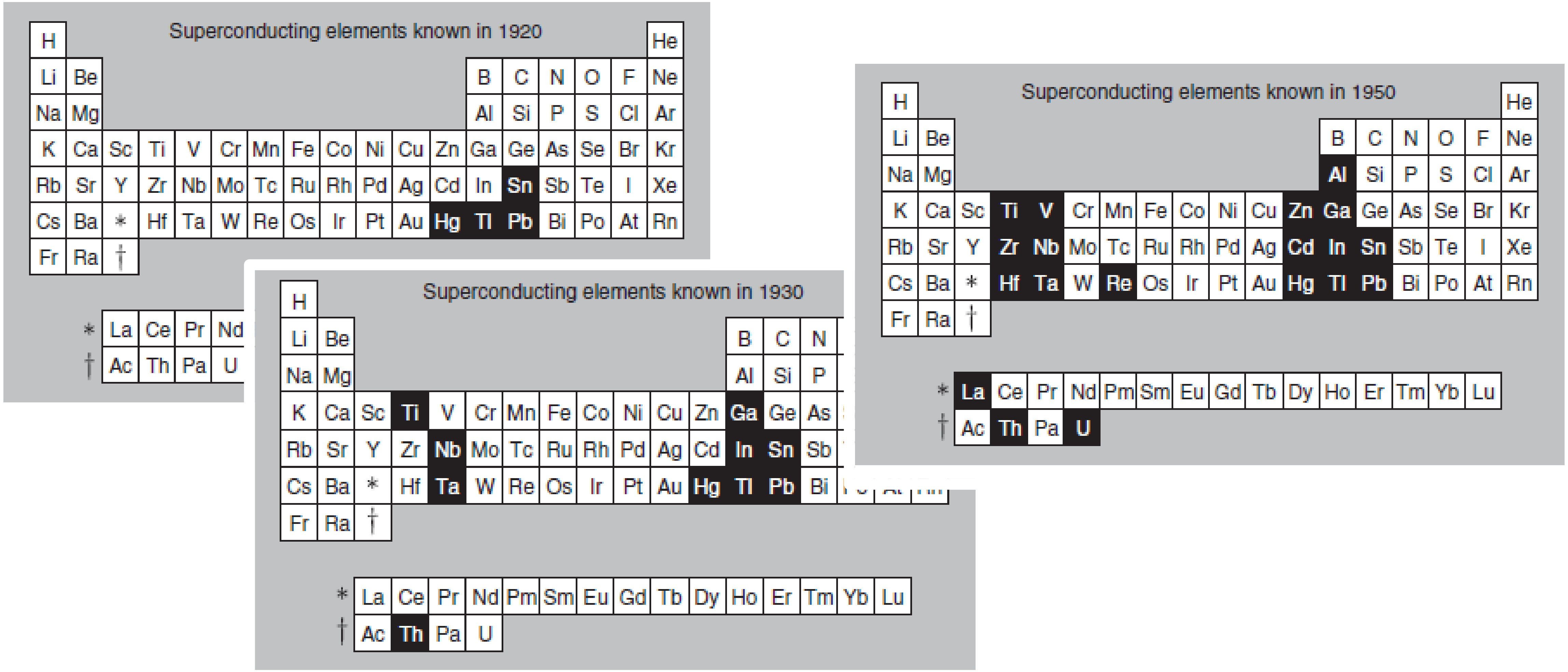
*	La	Ce	Pr	Nd
†	Ac	Th	Pa	U

Superconducting elements known in 1930

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	**Ti**	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	**Ga**	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	**Nb**	Mo	Tc	Ru	Rh	Pd	Ag	Cd	**In**	**Sn**	Sb	Te	I	Xe
Cs	Ba	*	Hf	**Ta**	W	Re	Os	Ir	Pt	Au	**Hg**	**Tl**	**Pb**	Bi	Po	At	Rn
Fr	Ra	†															

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†	Ac	**Th**	Pa	U											

Superconducting elements



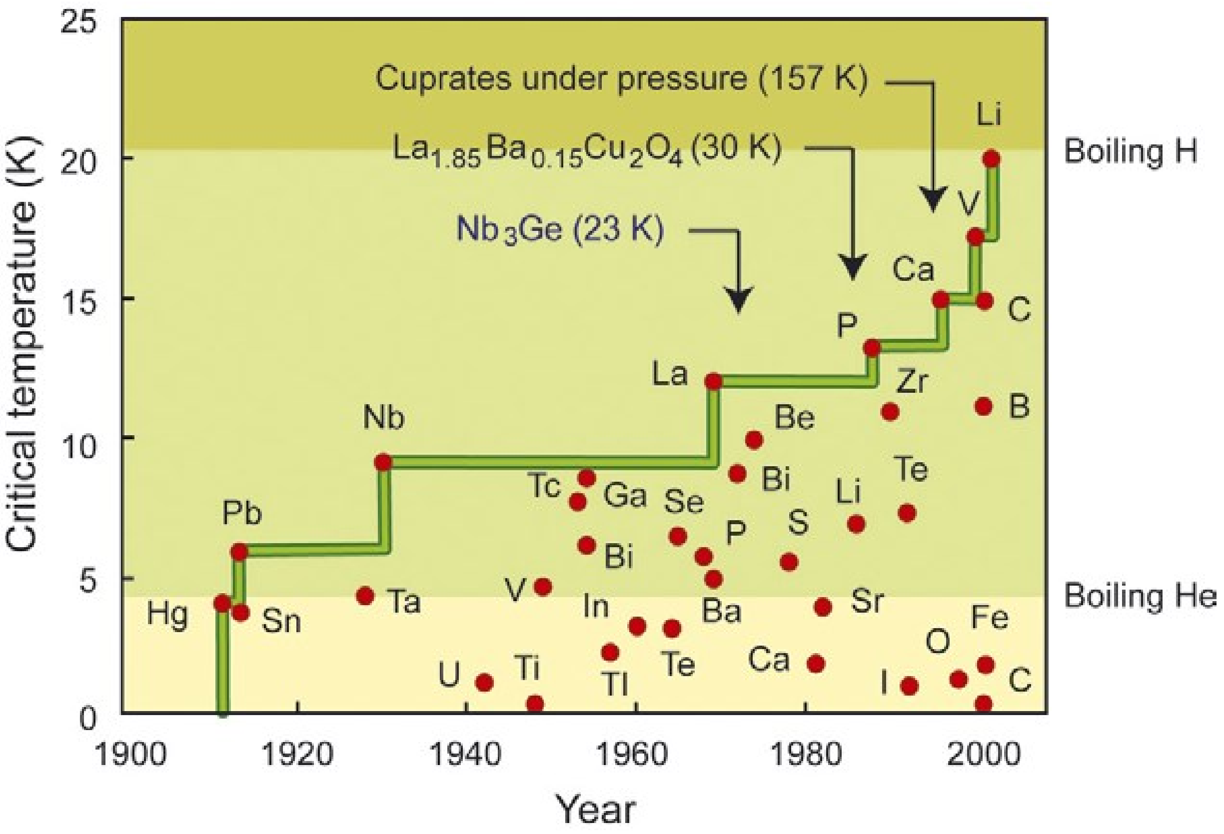
Superconducting elements known in 1920

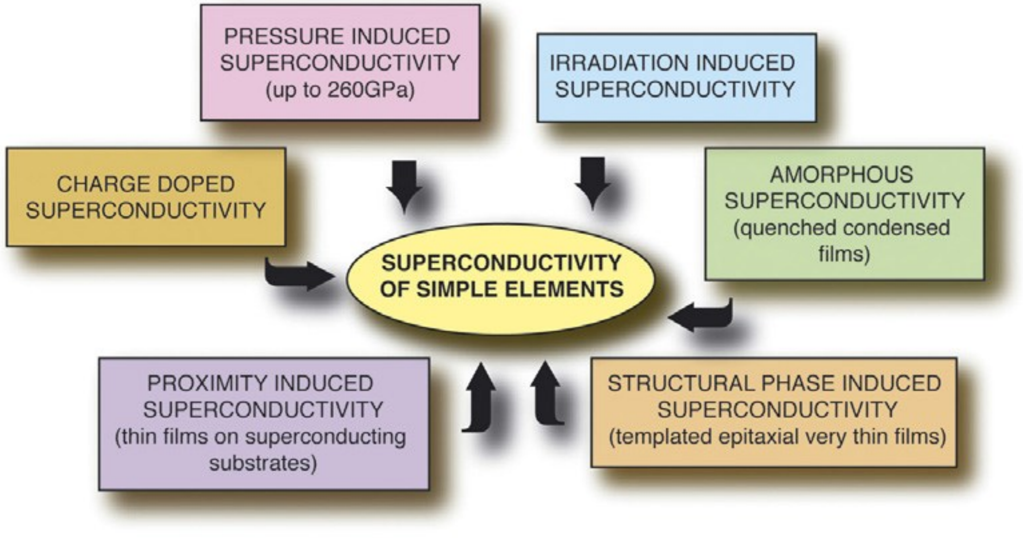
Superconducting elements known in 1930

Superconducting elements known in 1950

Superconducting elements

Historical development of the critical temperature of simple elements





PRESSURE INDUCED SUPERCONDUCTIVITY (up to 260GPa)

IRRADIATION INDUCED SUPERCONDUCTIVITY

CHARGE DOPED SUPERCONDUCTIVITY

AMORPHOUS SUPERCONDUCTIVITY (quenched condensed films)

SUPERCONDUCTIVITY OF SIMPLE ELEMENTS

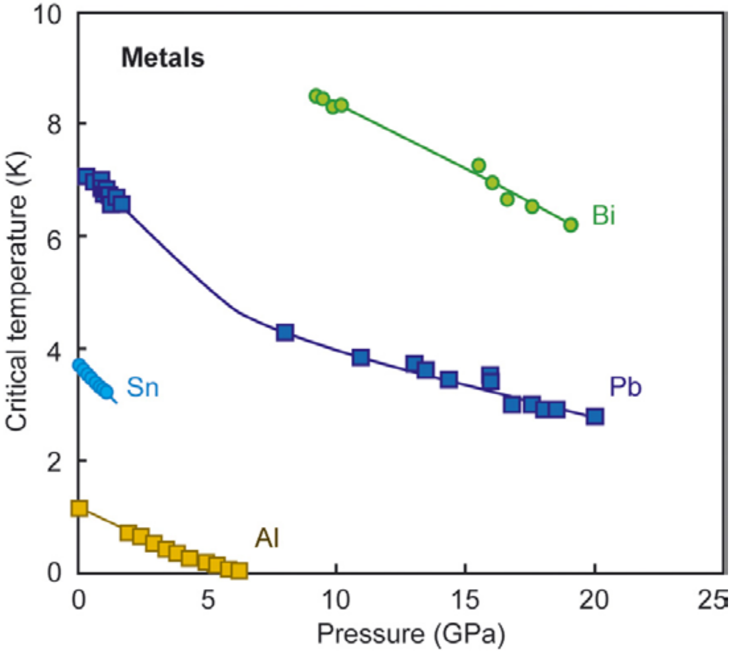
PROXIMITY INDUCED SUPERCONDUCTIVITY (thin films on superconducting substrates)

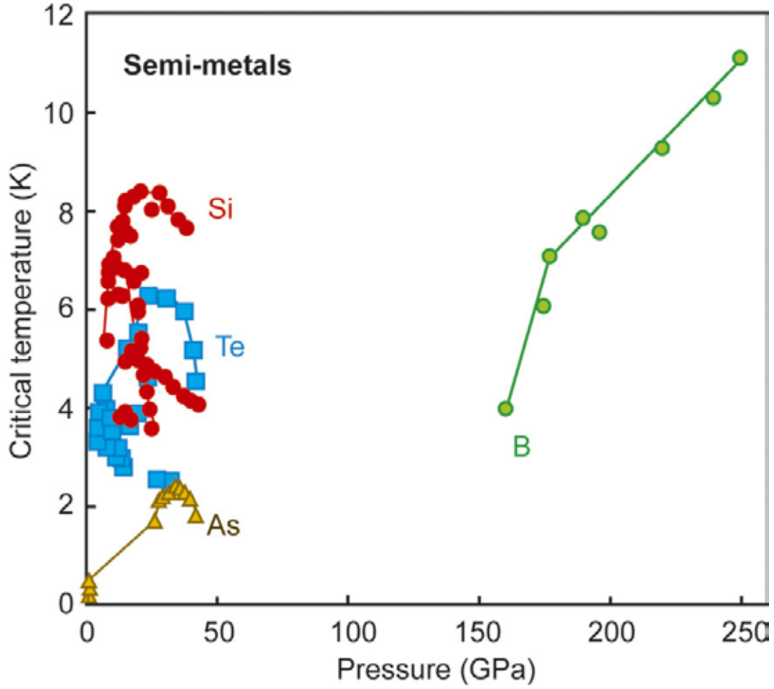
STRUCTURAL PHASE INDUCED SUPERCONDUCTIVITY (templated epitaxial very thin films)

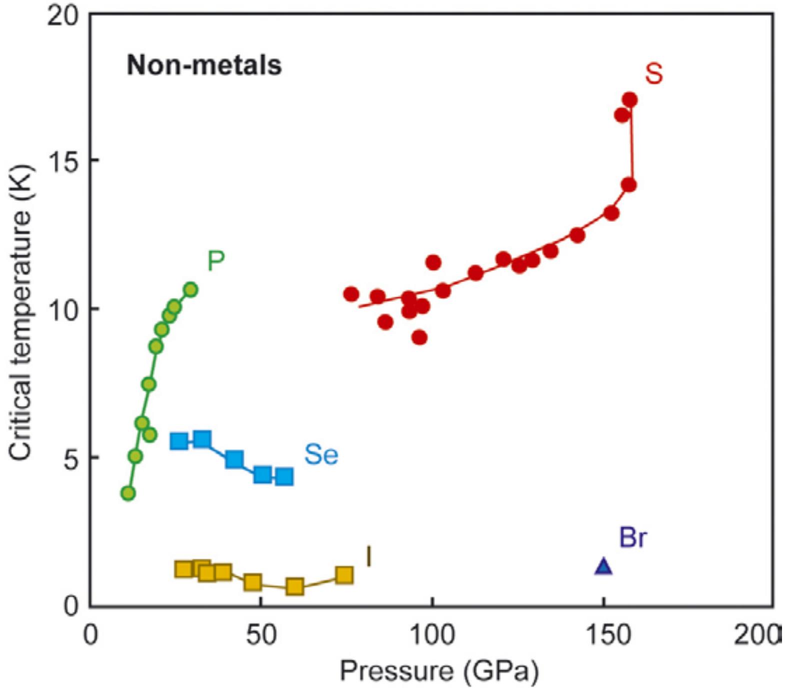
Techniques used to transform normal elements into superconductors

C. Buzea and K. Robbie, "Assembling the puzzle of superconducting elements: a review," Superconductor Science and Technology, vol. 18, Nov. 2004

Pressure effect

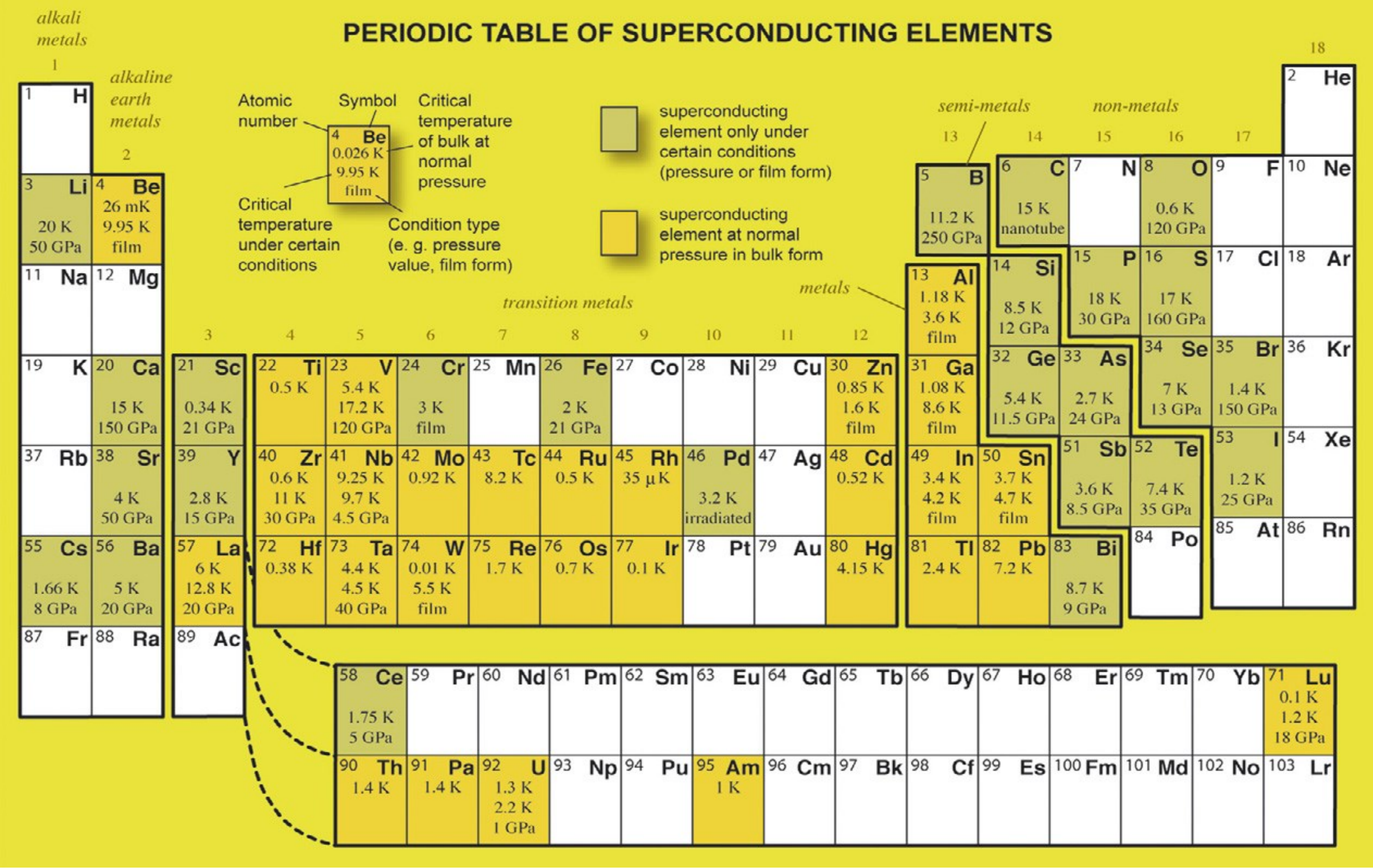






C. Buzea and K. Robbie, "Assembling the puzzle of superconducting elements: a review," Superconductor Science and Technology, vol. 18, Nov. 2004

Superconducting elements



PERIODIC TABLE OF SUPERCONDUCTING ELEMENTS

Atomic number — Symbol — Critical temperature of bulk at normal pressure
4 Be
0.026 K
9.95 K
film
Critical temperature under certain conditions — Condition type (e. g. pressure value, film form)

▨ superconducting element only under certain conditions (pressure or film form)

▨ superconducting element at normal pressure in bulk form

alkali metals · *alkaline earth metals* · *transition metals* · *metals* · *semi-metals* · *non-metals*

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li 20 K 50 GPa	4 Be 26 mK 9.95 K film											5 B 11.2 K 250 GPa	6 C 15 K nanotube	7 N	8 O 0.6 K 120 GPa	9 F	10 Ne
11 Na	12 Mg											13 Al 1.18 K 3.6 K film	14 Si 8.5 K 12 GPa	15 P 18 K 30 GPa	16 S 17 K 160 GPa	17 Cl	18 Ar
19 K	20 Ca 15 K 150 GPa	21 Sc 0.34 K 21 GPa	22 Ti 0.5 K	23 V 5.4 K 17.2 K 120 GPa	24 Cr 3 K film	25 Mn	26 Fe 2 K 21 GPa	27 Co	28 Ni	29 Cu	30 Zn 0.85 K 1.6 K film	31 Ga 1.08 K 8.6 K film	32 Ge 5.4 K 11.5 GPa	33 As 2.7 K 24 GPa	34 Se 7 K 13 GPa	35 Br 1.4 K 150 GPa	36 Kr
37 Rb	38 Sr 4 K 50 GPa	39 Y 2.8 K 15 GPa	40 Zr 0.6 K 11 K 30 GPa	41 Nb 9.25 K 9.7 K 4.5 GPa	42 Mo 0.92 K	43 Tc 8.2 K	44 Ru 0.5 K	45 Rh 35 µK	46 Pd 3.2 K irradiated	47 Ag	48 Cd 0.52 K	49 In 3.4 K 4.2 K film	50 Sn 3.7 K 4.7 K film	51 Sb 3.6 K 8.5 GPa	52 Te 7.4 K 35 GPa	53 I 1.2 K 25 GPa	54 Xe
55 Cs 1.66 K 8 GPa	56 Ba 5 K 20 GPa	57 La 6 K 12.8 K 20 GPa	72 Hf 0.38 K	73 Ta 4.4 K 4.5 K 40 GPa	74 W 0.01 K 5.5 K film	75 Re 1.7 K	76 Os 0.7 K	77 Ir 0.1 K	78 Pt	79 Au	80 Hg 4.15 K	81 Tl 2.4 K	82 Pb 7.2 K	83 Bi 8.7 K 9 GPa	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

58 Ce 1.75 K 5 GPa	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 0.1 K 1.2 K 18 GPa
90 Th 1.4 K	91 Pa 1.4 K	92 U 1.3 K 2.2 K 1 GPa	93 Np	94 Pu	95 Am 1 K	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

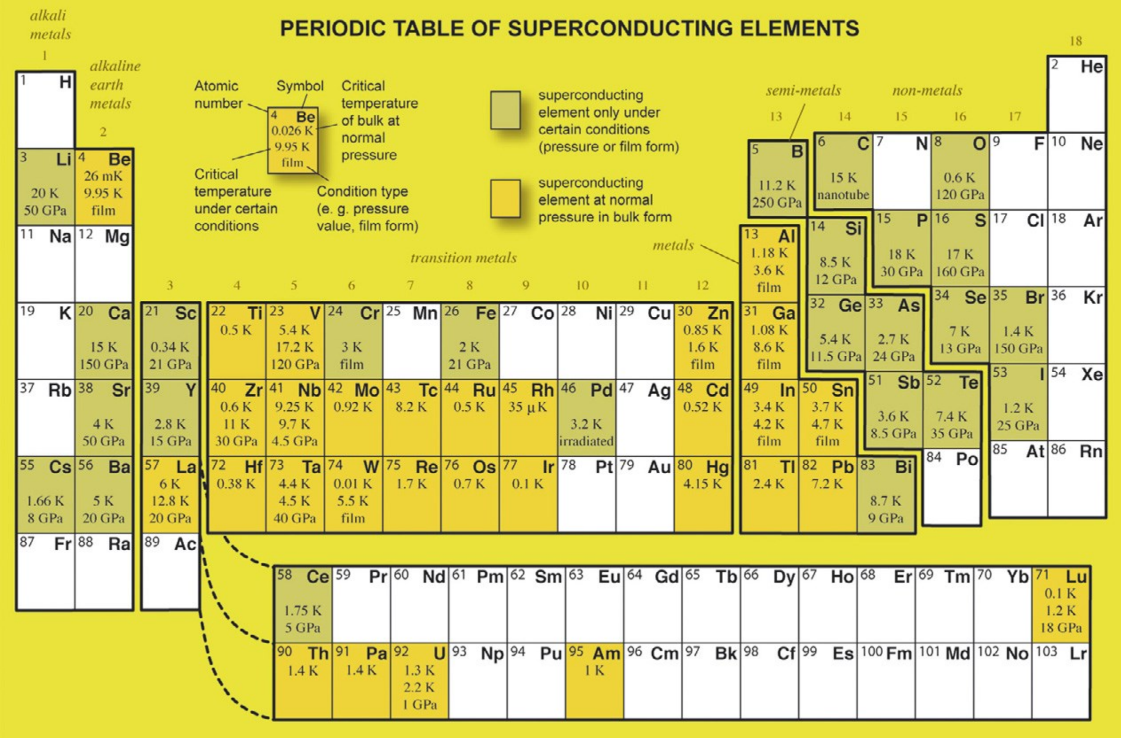
C. Buzea and K. Robbie, "Assembling the puzzle of superconducting elements: a review," Superconductor Science and Technology, vol. 18, Nov. 2004

SC Elements considerations

Two groups of SC

*The **non-transition metals** – to these belong most of the superconducting high-pressure phases*

*The **transition metals** – with increasing element number, an inner shell (3d, 4d, and 5d levels; for the lanthanides and actinides, the 4f and 5f levels) becomes filled up within a row*

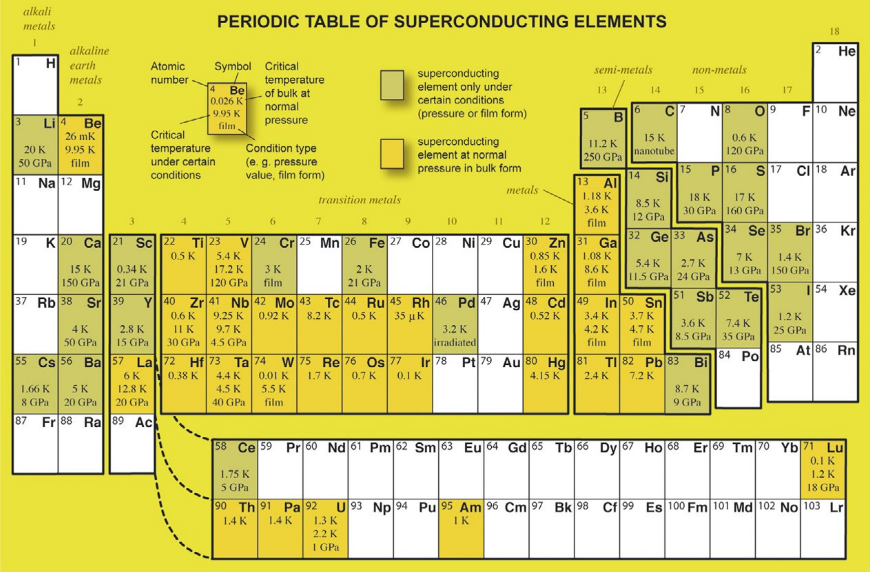


SC Elements considerations (2)

Superconductivity is **not a rare property of metals**

Superconductivity is **neither found** in the **magnetic compounds, nor in the noble metals or Cu**

This indicates that **superconductivity is incompatible with magnetism**, and **absent in metals with the highest electrical conductivity**



PERIODIC TABLE OF SUPERCONDUCTING ELEMENTS

▨ superconducting element only under certain conditions (pressure or film form)

🟨 superconducting element at normal pressure in bulk form

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li 20 K 50 GPa	4 Be 26 mK 9.95 K film											5 B 11.2 K 250 GPa	6 C 15 K nanotube	7 N	8 O 0.6 K 120 GPa	9 F	10 Ne
11 Na	12 Mg											13 Al 1.18 K 3.6 K film	14 Si 8.5 K 12 GPa	15 P 18 K 30 GPa	16 S 17 K 160 GPa	17 Cl	18 Ar
19 K	20 Ca 15 K 150 GPa	21 Sc 0.34 K 21 GPa	22 Ti 0.5 K	23 V 5.4 K 17.2 K 120 GPa	24 Cr 3 K film	25 Mn	26 Fe 2 K 21 GPa	27 Co	28 Ni	29 Cu	30 Zn 0.85 K 1.6 K film	31 Ga 1.08 K 8.6 K film	32 Ge 5.4 K 11.5 GPa	33 As 2.7 K 24 GPa	34 Se 7 K 13 GPa	35 Br 1.4 K 150 GPa	36 Kr
37 Rb	38 Sr 4 K 50 GPa	39 Y 2.8 K 15 GPa	40 Zr 0.6 K 11 K 30 GPa	41 Nb 9.25 K 9.7 K 4.5 GPa	42 Mo 0.92 K	43 Tc 8.2 K	44 Ru 0.5 K	45 Rh 35 µK	46 Pd 3.2 K irradiated	47 Ag	48 Cd 0.52 K	49 In 3.4 K 4.2 K film	50 Sn 3.7 K 4.7 K film	51 Sb 3.6 K 8.5 GPa	52 Te 7.4 K 35 GPa	53 I 1.2 K 25 GPa	54 Xe
55 Cs 1.66 K 8 GPa	56 Ba 5 K 20 GPa	57 La 6 K 12.8 K 20 GPa	72 Hf 0.38 K	73 Ta 4.4 K 4.5 K 40 GPa	74 W 0.01 K 5.5 K film	75 Re 1.7 K	76 Os 0.7 K	77 Ir 0.1 K	78 Pt	79 Au	80 Hg 4.15 K	81 Tl 2.4 K	82 Pb 7.2 K	83 Bi 8.7 K 9 GPa	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

58 Ce 1.75 K 5 GPa	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 0.1 K 1.2 K 18 GPa
90 Th 1.4 K	91 Pa 1.4 K	92 U 1.3 K 2.2 K 1 GPa	93 Np	94 Pu	95 Am 1 K	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

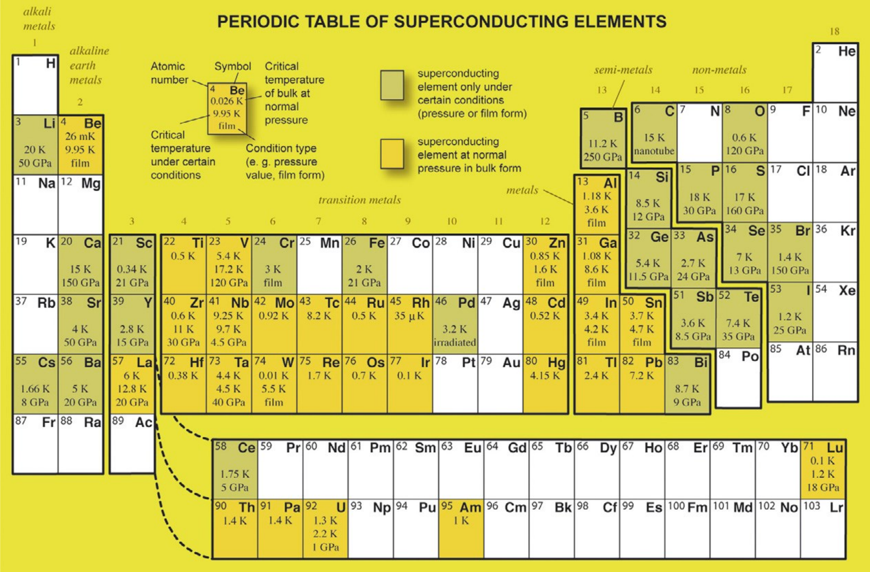
BCS theory explain these two facts:

SC Elements considerations (2)

Superconductivity is **not a rare property of metals**

Superconductivity is **neither found** in the **magnetic compounds, nor in the noble metals or Cu**

This indicates that **superconductivity is incompatible with magnetism**, and **absent in metals with the highest electrical conductivity**



PERIODIC TABLE OF SUPERCONDUCTING ELEMENTS

superconducting element only under certain conditions (pressure or film form)

superconducting element at normal pressure in bulk form

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li 20 K 50 GPa	4 Be 26 mK 9.95 K film											5 B 11.2 K 250 GPa	6 C 15 K nanotube	7 N	8 O 0.6 K 120 GPa	9 F	10 Ne
11 Na	12 Mg											13 Al 1.18 K 3.6 K film	14 Si 8.5 K 12 GPa	15 P 18 K 30 GPa	16 S 17 K 160 GPa	17 Cl	18 Ar
19 K	20 Ca 15 K 150 GPa	21 Sc 0.34 K 21 GPa	22 Ti 0.5 K	23 V 5.4 K 17.2 K 120 GPa	24 Cr 3 K film	25 Mn	26 Fe 2 K 21 GPa	27 Co	28 Ni	29 Cu	30 Zn 0.85 K 1.6 K film	31 Ga 1.08 K 8.6 K film	32 Ge 5.4 K 11.5 GPa	33 As 2.7 K 24 GPa	34 Se 7 K 13 GPa	35 Br 1.4 K 150 GPa	36 Kr
37 Rb	38 Sr 4 K 50 GPa	39 Y 2.8 K 15 GPa	40 Zr 0.6 K 11 K 30 GPa	41 Nb 9.25 K 9.7 K 4.5 GPa	42 Mo 0.92 K	43 Tc 8.2 K	44 Ru 0.5 K	45 Rh 35 µK	46 Pd 3.2 K irradiated	47 Ag	48 Cd 0.52 K	49 In 3.4 K 4.2 K film	50 Sn 3.7 K 4.7 K film	51 Sb 3.6 K 8.5 GPa	52 Te 7.4 K 35 GPa	53 I 1.2 K 25 GPa	54 Xe
55 Cs 1.66 K 8 GPa	56 Ba 5 K 20 GPa	57 La 6 K 12.8 K 20 GPa	72 Hf 0.38 K	73 Ta 4.4 K 4.5 K 40 GPa	74 W 0.01 K 5.5 K film	75 Re 1.7 K	76 Os 0.7 K	77 Ir 0.1 K	78 Pt	79 Au	80 Hg 4.15 K	81 Tl 2.4 K	82 Pb 7.2 K	83 Bi 8.7 K 9 GPa	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

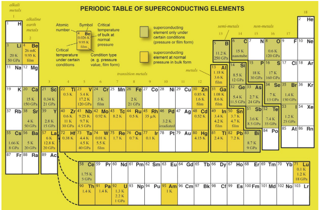
58 Ce 1.75 K 5 GPa	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu 0.1 K 1.2 K 18 GPa
90 Th 1.4 K	91 Pa 1.4 K	92 U 1.3 K 2.2 K 1 GPa	93 Np	94 Pu	95 Am 1 K	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

BCS theory explain these two facts:

1. excellent electrical conductivity is a signature of weak electron–phonon interaction

2. magnetism breaks up the Cooper-pairs

SC Elements considerations (3)

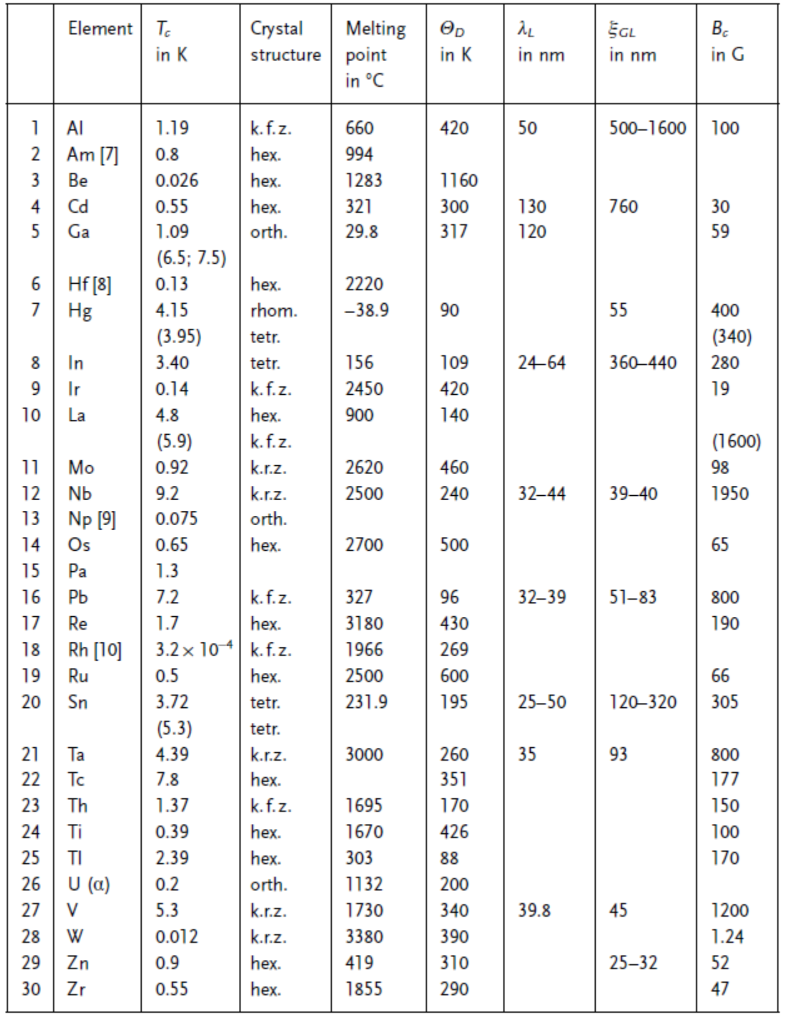


The statement that “**all metals become superconducting at sufficiently low temperatures**” cannot, in principle, be disproved:

1. **difficult to find SC with Tc < 10^{-2} K;**
2. example of highly dilute alloys of the noble metals
   (Au shows Tc of 0,2 mK and Cu of 10^{-6} mK);
3. example of a non-magnetic high-pressure phase of iron can become
   superconducting with a transition temperature up to 2 K

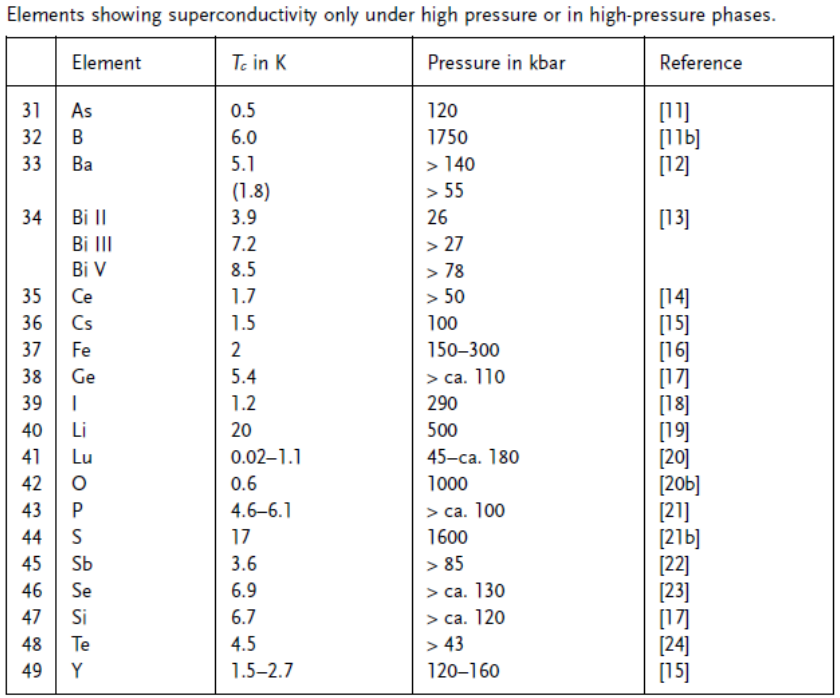
SC Elements considerations (4)

There is **no correlation** apparent **between** the value of the **Tc** and **other characteristic properties**



	Element	T_c in K	Crystal structure	Melting point in °C	Θ_D in K	λ_L in nm	ξ_{GL} in nm	B_c in G
1	Al	1.19	k. f. z.	660	420	50	500–1600	100
2	Am [7]	0.8	hex.	994				
3	Be	0.026	hex.	1283	1160			
4	Cd	0.55	hex.	321	300	130	760	30
5	Ga	1.09	orth.	29.8	317	120		59
		(6.5; 7.5)						
6	Hf [8]	0.13	hex.	2220				
7	Hg	4.15	rhom.	–38.9	90		55	400
		(3.95)	tetr.					(340)
8	In	3.40	tetr.	156	109	24–64	360–440	280
9	Ir	0.14	k. f. z.	2450	420			19
10	La	4.8	hex.	900	140			
		(5.9)	k. f. z.					(1600)
11	Mo	0.92	k.r.z.	2620	460			98
12	Nb	9.2	k.r.z.	2500	240	32–44	39–40	1950
13	Np [9]	0.075	orth.					
14	Os	0.65	hex.	2700	500			65
15	Pa	1.3						
16	Pb	7.2	k. f. z.	327	96	32–39	51–83	800
17	Re	1.7	hex.	3180	430			190
18	Rh [10]	3.2×10^{-4}	k. f. z.	1966	269			
19	Ru	0.5	hex.	2500	600			66
20	Sn	3.72	tetr.	231.9	195	25–50	120–320	305
		(5.3)	tetr.					
21	Ta	4.39	k.r.z.	3000	260	35	93	800
22	Tc	7.8	hex.		351			177
23	Th	1.37	k. f. z.	1695	170			150
24	Ti	0.39	hex.	1670	426			100
25	Tl	2.39	hex.	303	88			170
26	U (α)	0.2	orth.	1132	200			
27	V	5.3	k.r.z.	1730	340	39.8	45	1200
28	W	0.012	k.r.z.	3380	390			1.24
29	Zn	0.9	hex.	419	310		25–32	52
30	Zr	0.55	hex.	1855	290			47

Possible correlation between SC and the volume occupied by an atom within the metallic crystal (small volume is better for SC)



Elements showing superconductivity only under high pressure or in high-pressure phases.

	Element	T_c in K	Pressure in kbar	Reference
31	As	0.5	120	[11]
32	B	6.0	1750	[11b]
33	Ba	5.1	> 140	[12]
		(1.8)	> 55	
34	Bi II	3.9	26	[13]
	Bi III	7.2	> 27	
	Bi V	8.5	> 78	
35	Ce	1.7	> 50	[14]
36	Cs	1.5	100	[15]
37	Fe	2	150–300	[16]
38	Ge	5.4	> ca. 110	[17]
39	I	1.2	290	[18]
40	Li	20	500	[19]
41	Lu	0.02–1.1	45–ca. 180	[20]
42	O	0.6	1000	[20b]
43	P	4.6–6.1	> ca. 100	[21]
44	S	17	1600	[21b]
45	Sb	3.6	> 85	[22]
46	Se	6.9	> ca. 130	[23]
47	Si	6.7	> ca. 120	[17]
48	Te	4.5	> 43	[24]
49	Y	1.5–2.7	120–160	[15]

Superconducting elements, their crystal structure and melting point, and some properties of the superconducting state: transition temperature Tc, Debye temperature QD, London penetration depth λ, Ginzburg-Landau coherence length ξ_{GL}, and critical magnetic field B_c. The transition temperatures shown in brackets belong to additional crystal modifications. Many of the entries can only be taken as an indication

Kammerlingh Onnes's visions

Construction of a 10 T Magnet with Hg and Pb Wires

Presented at 3rd International Congress of Refrigeration, Chicago 1913

- Experiments with Hg and Pb wires failed
- The coil lost superconducting properties already at small Current densities and at Magnetic Fields of several 100 Gauss
- The experiment ended with a disappointment and was terminated


1st Pb wire coil 1912

The breakthrough only came decades later (1961)

SC alloys

No pratical use of Superconductors untill the discovery of SC alloys

In 1931, W. J. de Haas and W. H. Keesom, discovered SC in an alloy

In 1941 NbN (Tc = 15K) and NbC (Tc = 16K) were discovered
Nb seems a good candidate for great SC alloys…

In 1953 Hardy and Huulm reported **Tc=17 K in V_3Si** and discovered a **new class of SC: A15** (aka **β-tungsten structure**)

In 1954, Mathias et al. reported **Tc=18 K in Nb_3Sn**

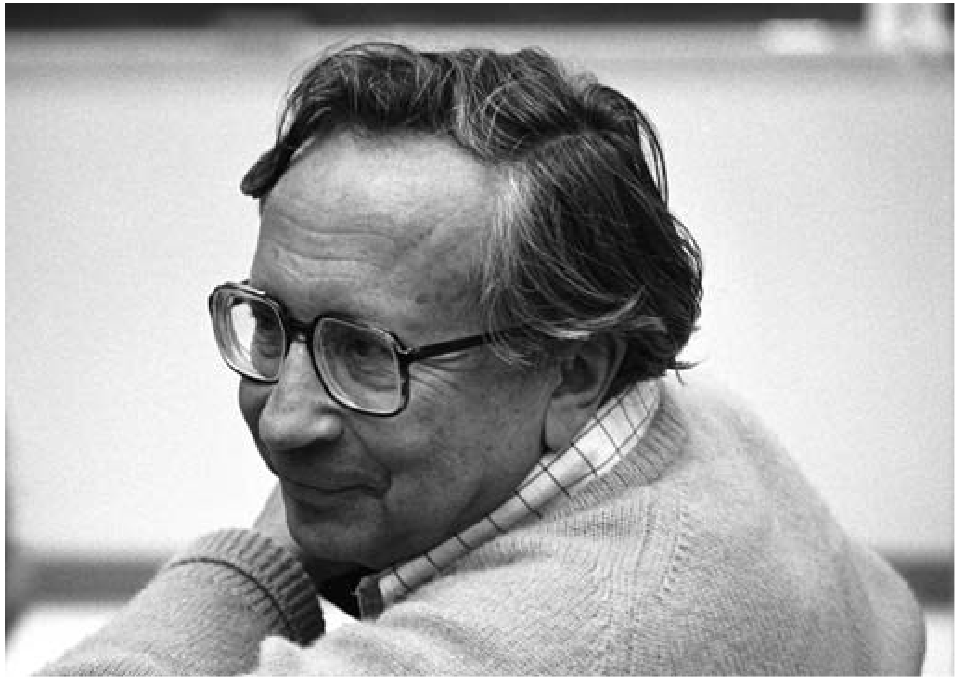
In 1954 George Yntema at Illinois built a magnet out of Nb wire that reached 0.3 tesla

In 1960, with Nb_3Sn was realized the first electromagnets to exceed 1 tesla (9 T)

Mathias rules

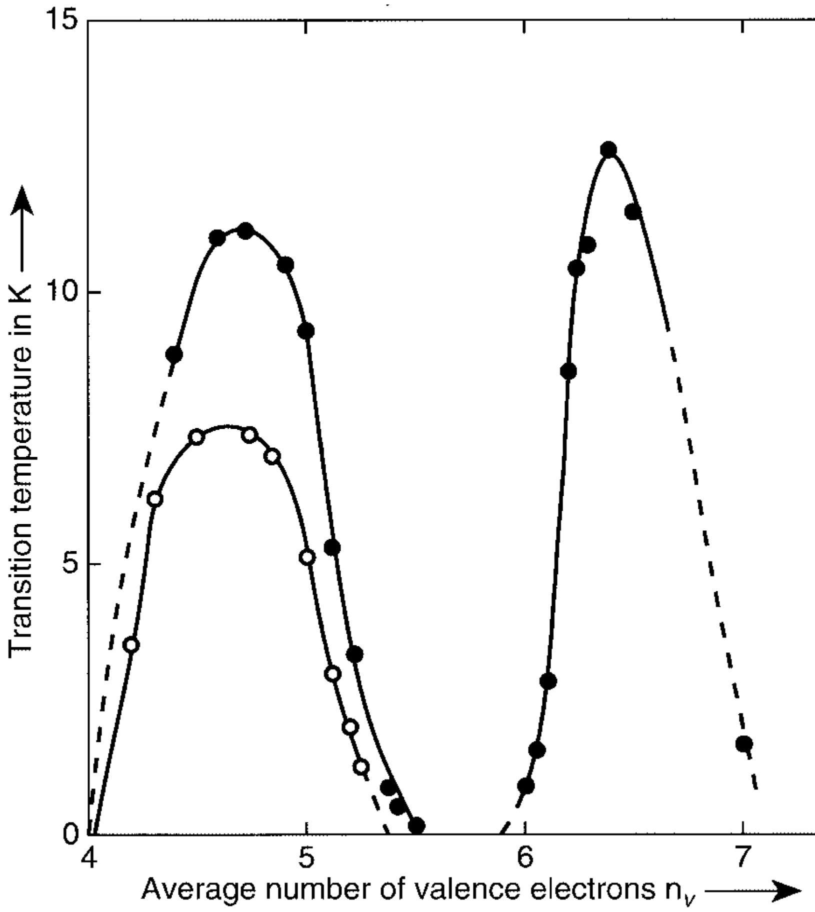
Mathias groups **discovered hundreds of new SC** following **6 simple rules**…

1. **High symmetry** is a good thing, cubic symmetry is best
2. **High density of electronic states** is a good thing
3. **Stay away** from **oxygen**
4. **Stay away** from **magnetism**
5. **Stay away** from **insulators**
6. ***Stay away*** *from* ***theoretical physicists!***



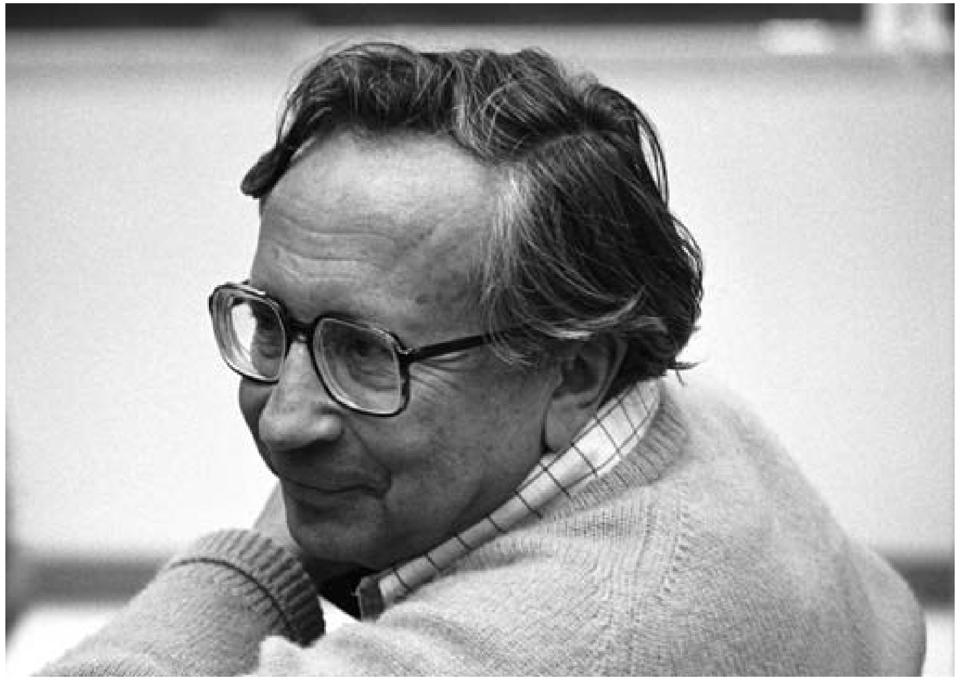
Bernd Matthias

Valence electrons role



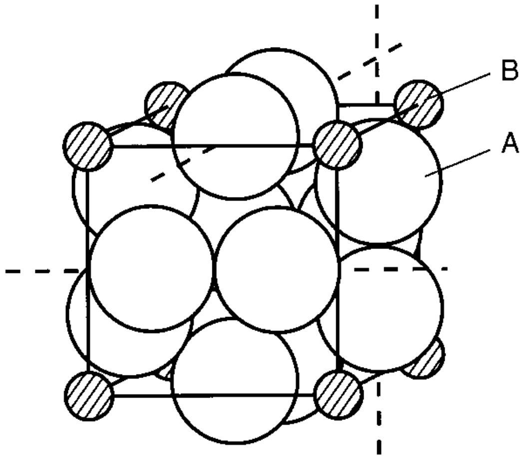
Transition temperature of some alloys of the transition metals plotted versus the average number of valence electrons solid dots, Zr-Nb-Mo-Re; open circles, Ti-V-Cr.

Matthias indicates that the **average number of valence electrons** of a material represents a **key to superconductivity**

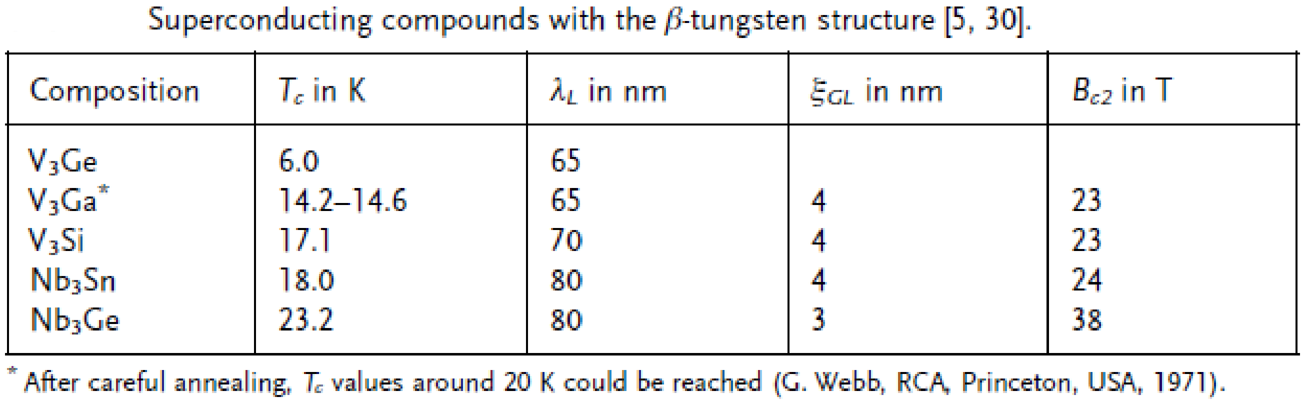


Bernd Matthias

A15 Superconductors



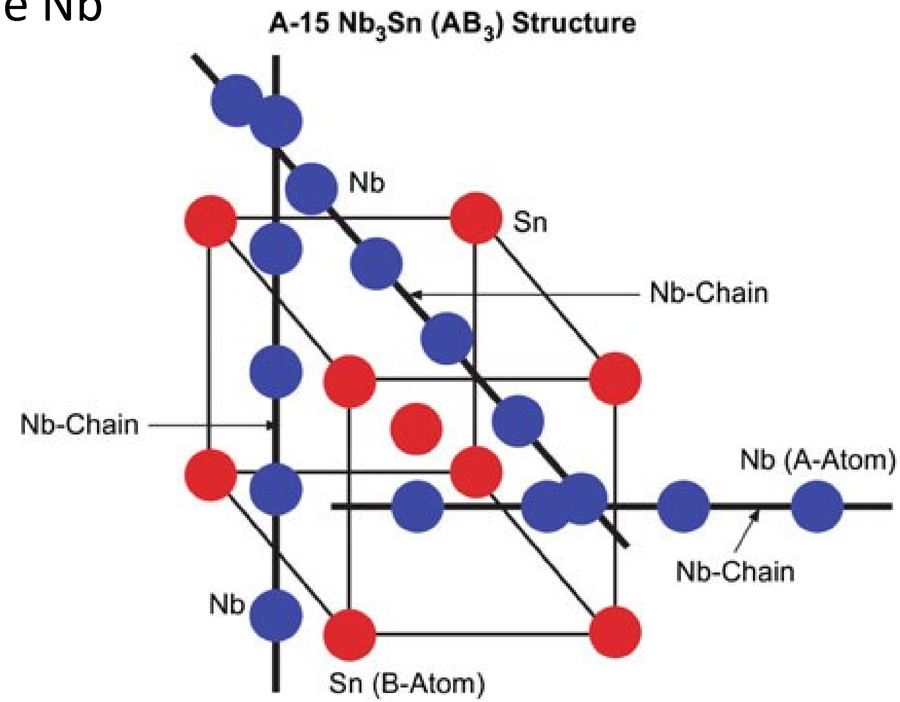
The arrangement of the A atoms (Nb) along the chains parallel to the *x*, *y*, and *z* axes is highly characteristic. The orthogonal chains do not intersect. Within the chains, the A atoms (Nb) have a smaller mutual distance than in the lattice of pure Nb



Superconducting compounds with the β-tungsten structure [5, 30].

Composition	T_c in K	λ_L in nm	ξ_{GL} in nm	B_{c2} in T
V_3Ge	6.0	65		
V_3Ga^*	14.2–14.6	65	4	23
V_3Si	17.1	70	4	23
Nb_3Sn	18.0	80	4	24
Nb_3Ge	23.2	80	3	38

* After careful annealing, T_c values around 20 K could be reached (G. Webb, RCA, Princeton, USA, 1971).



Organic Superconductors

Discovered in 1975

Predicted in 1964 by Little, suggesting possibility to have room temperature SC due to Polaron mechanism instead of BCS one

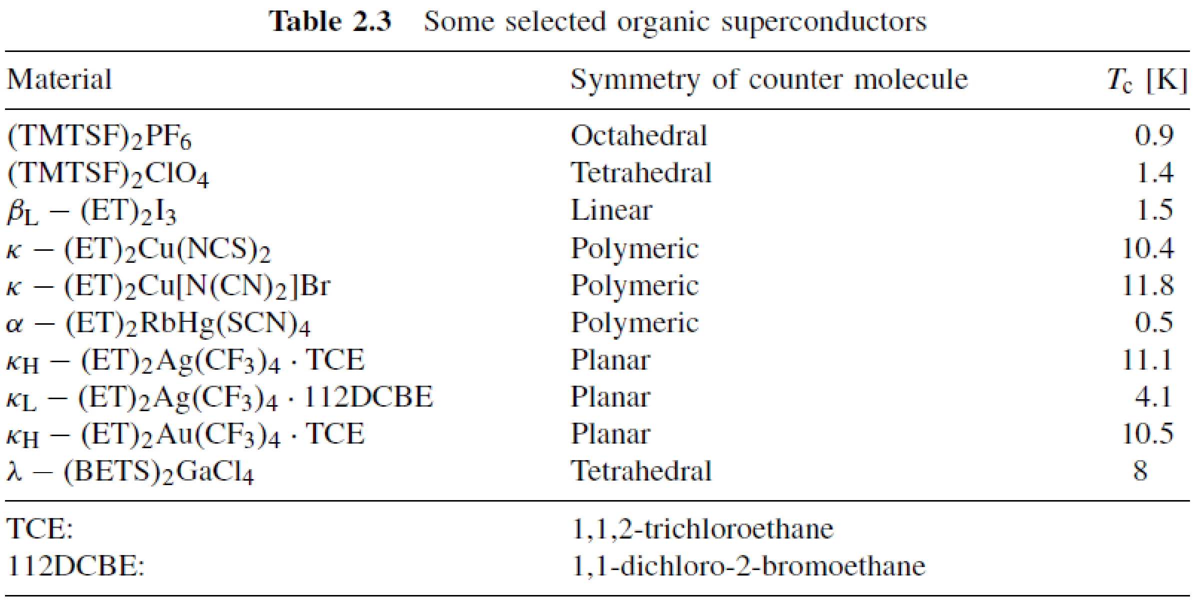
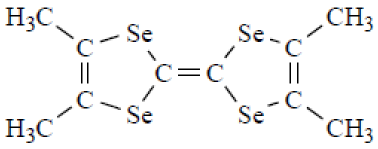
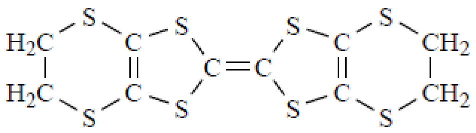
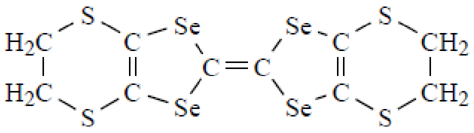


Table 2.3 Some selected organic superconductors

Material	Symmetry of counter molecule	T_c [K]
$(TMTSF)_2PF_6$	Octahedral	0.9
$(TMTSF)_2ClO_4$	Tetrahedral	1.4
$\beta_L - (ET)_2I_3$	Linear	1.5
$\kappa - (ET)_2Cu(NCS)_2$	Polymeric	10.4
$\kappa - (ET)_2Cu[N(CN)_2]Br$	Polymeric	11.8
$\alpha - (ET)_2RbHg(SCN)_4$	Polymeric	0.5
$\kappa_H - (ET)_2Ag(CF_3)_4 \cdot TCE$	Planar	11.1
$\kappa_L - (ET)_2Ag(CF_3)_4 \cdot 112DCBE$	Planar	4.1
$\kappa_H - (ET)_2Au(CF_3)_4 \cdot TCE$	Planar	10.5
$\lambda - (BETS)_2GaCl_4$	Tetrahedral	8
TCE:	1,1,2-trichloroethane	
112DCBE:	1,1-dichloro-2-bromoethane	

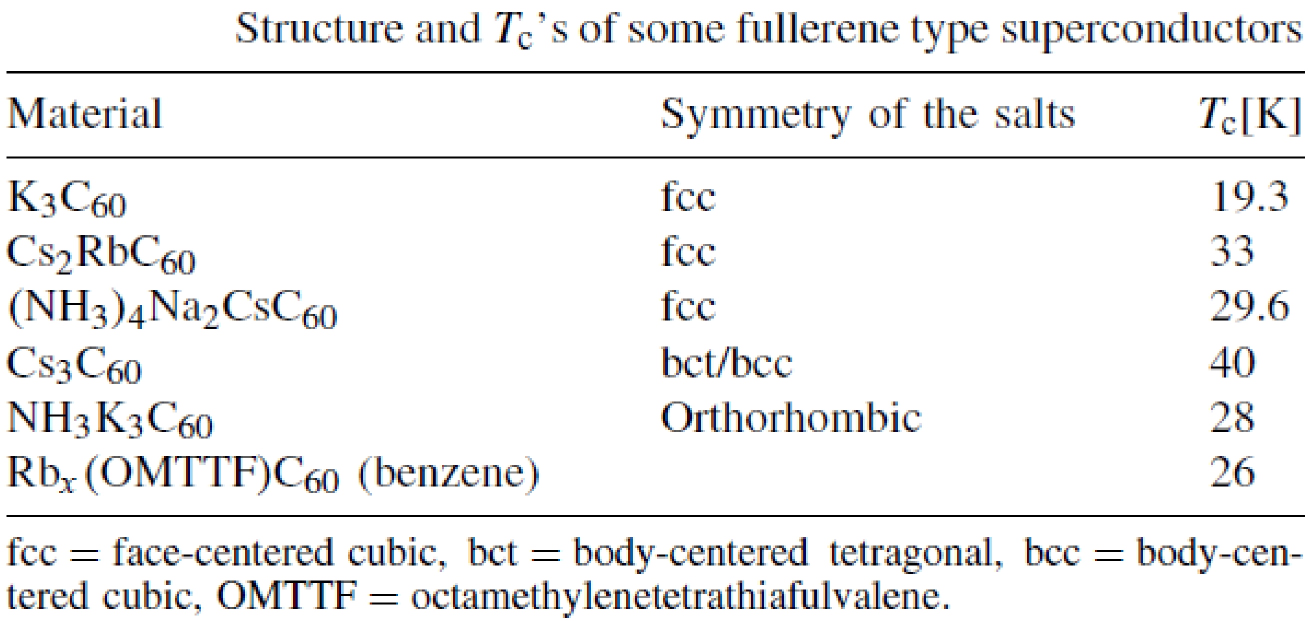

TMTSF


ET (BEDT-TTF)


BETS (BEDT-TSF)

Organic Superconductors (2)

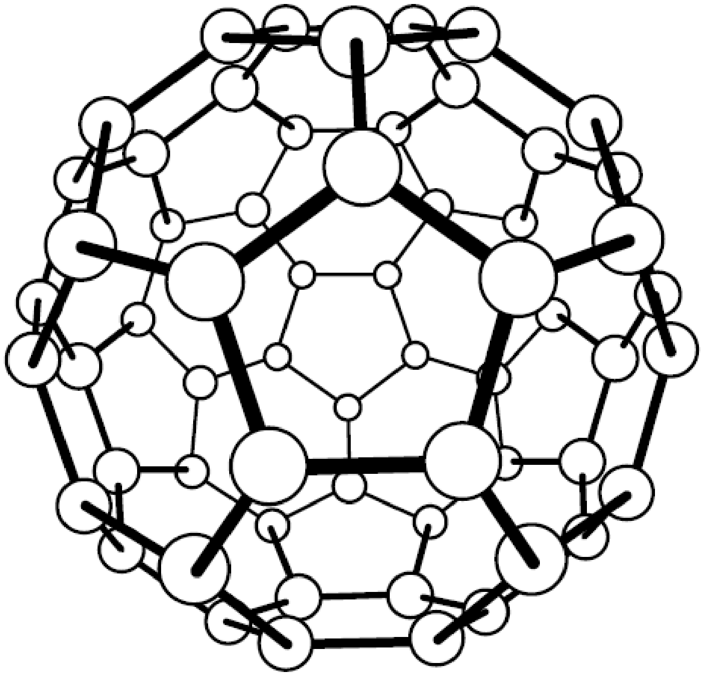
Fullerene Superconductors



Structure and T_c's of some fullerene type superconductors

Material	Symmetry of the salts	T_c[K]
K_3C_{60}	fcc	19.3
Cs_2RbC_{60}	fcc	33
$(NH_3)_4Na_2CsC_{60}$	fcc	29.6
Cs_3C_{60}	bct/bcc	40
$NH_3K_3C_{60}$	Orthorhombic	28
$Rb_x(OMTTF)C_{60}$ (benzene)		26

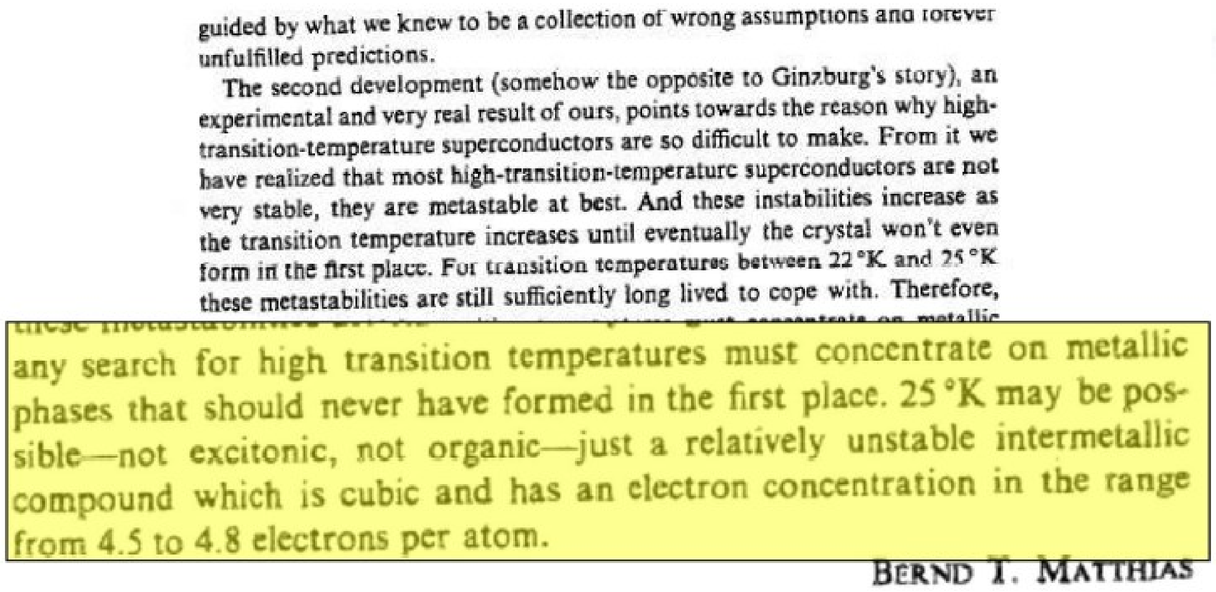
fcc = face-centered cubic, bct = body-centered tetragonal, bcc = body-centered cubic, OMTTF = octamethylenetetrathiafulvalene.



High Tc Superconductors?

BCS predicts for **Tc** values **below 20 K**

Some organic compounds become SC at high pressures

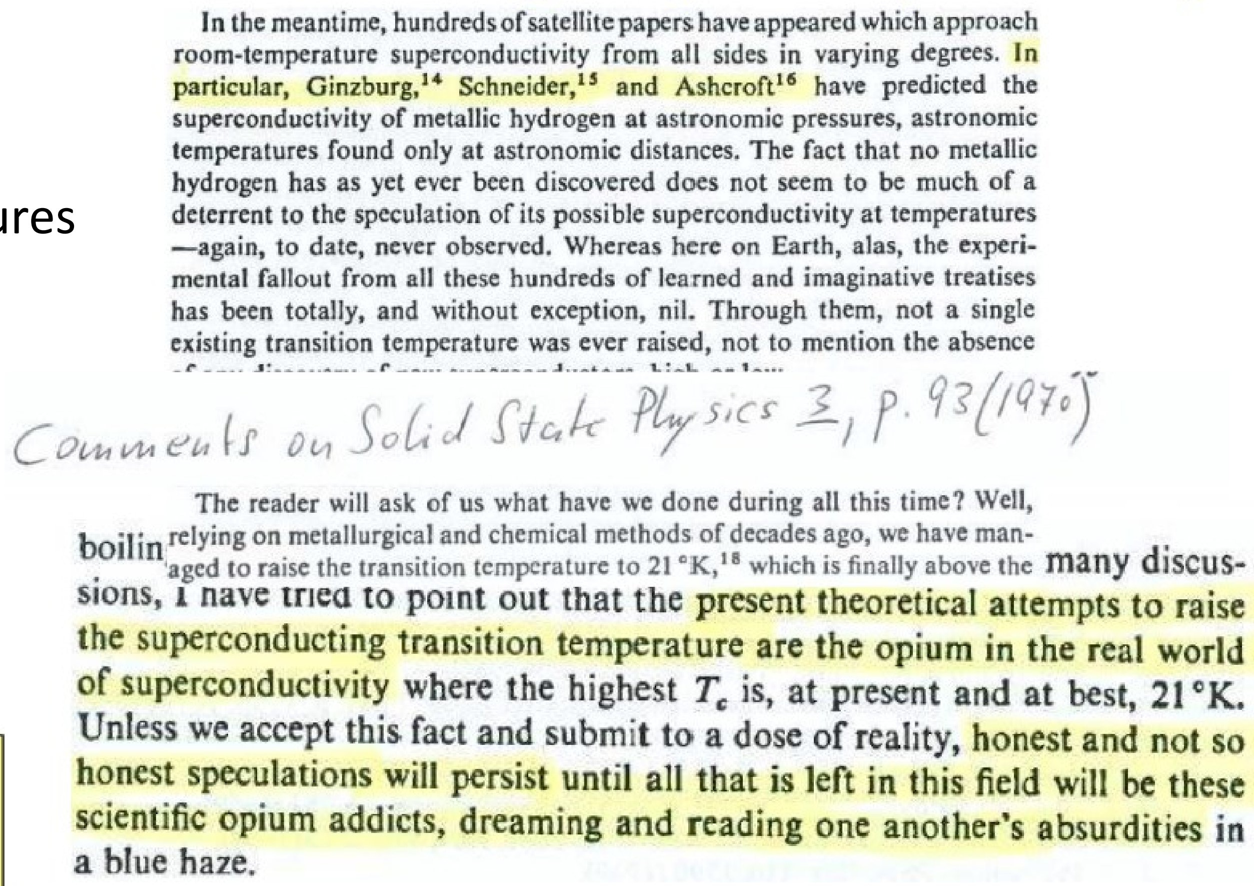


guided by what we knew to be a collection of wrong assumptions and forever unfulfilled predictions.

The second development (somehow the opposite to Ginzburg's story), an experimental and very real result of ours, points towards the reason why high-transition-temperature superconductors are so difficult to make. From it we have realized that most high-transition-temperature superconductors are not very stable, they are metastable at best. And these instabilities increase as the transition temperature increases until eventually the crystal won't even form in the first place. For transition temperatures between 22 °K and 25 °K these metastabilities are still sufficiently long lived to cope with. Therefore,

any search for high transition temperatures must concentrate on metallic phases that should never have formed in the first place. 25 °K may be possible—not excitonic, not organic—just a relatively unstable intermetallic compound which is cubic and has an electron concentration in the range from 4.5 to 4.8 electrons per atom.

BERND T. MATTHIAS



In the meantime, hundreds of satellite papers have appeared which approach room-temperature superconductivity from all sides in varying degrees. In particular, Ginzburg,[14] Schneider,[15] and Ashcroft[16] have predicted the superconductivity of metallic hydrogen at astronomic pressures, astronomic temperatures found only at astronomic distances. The fact that no metallic hydrogen has as yet ever been discovered does not seem to be much of a deterrent to the speculation of its possible superconductivity at temperatures—again, to date, never observed. Whereas here on Earth, alas, the experimental fallout from all these hundreds of learned and imaginative treatises has been totally, and without exception, nil. Through them, not a single existing transition temperature was ever raised, not to mention the absence

Comments on Solid State Physics 3, p. 93 (1970)

The reader will ask of us what have we done during all this time? Well, relying on metallurgical and chemical methods of decades ago, we have managed to raise the transition temperature to 21 °K,[18] which is finally above the

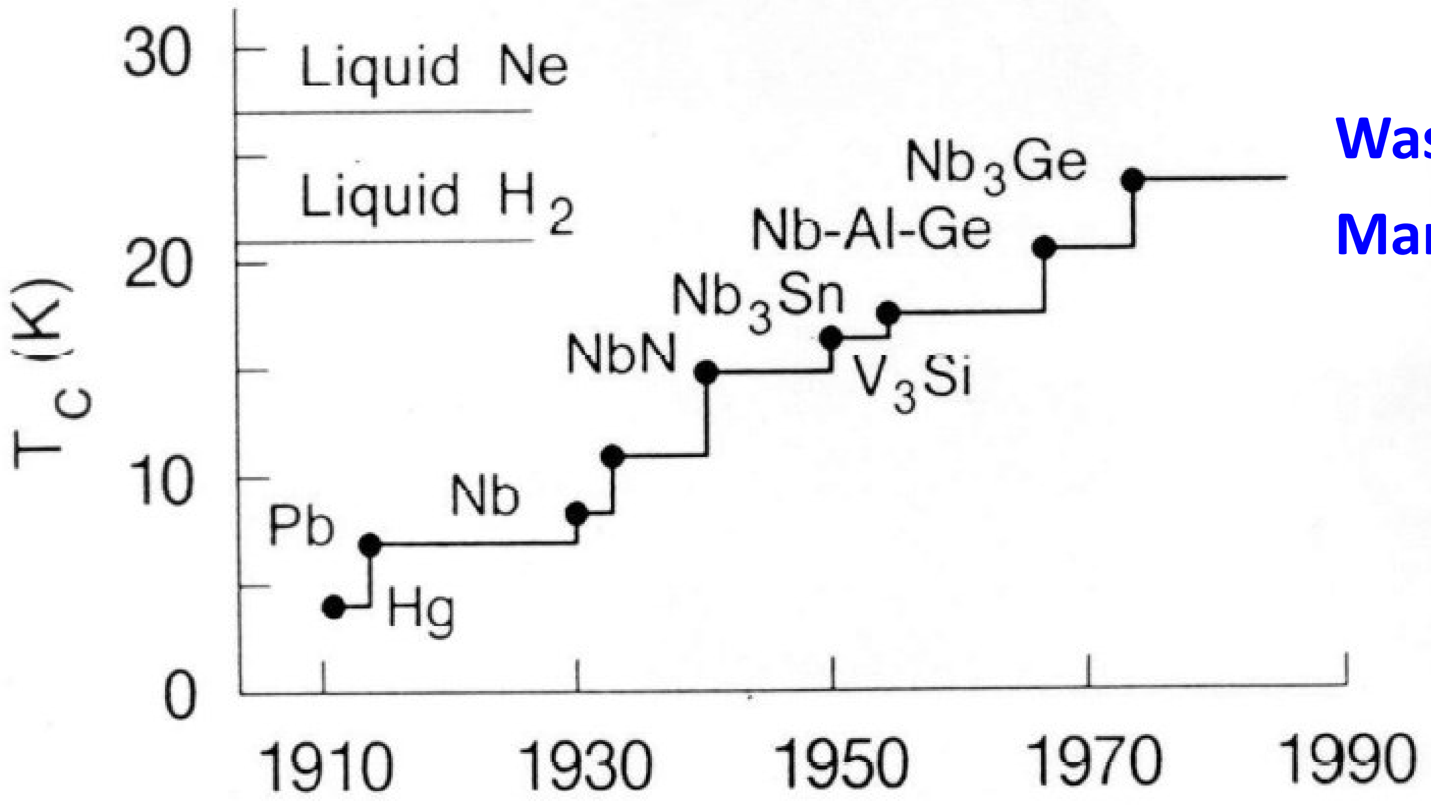
boilin many discussions, I have tried to point out that the present theoretical attempts to raise the superconducting transition temperature are the opium in the real world of superconductivity where the highest T_c is, at present and at best, 21 °K. Unless we accept this fact and submit to a dose of reality, honest and not so honest speculations will persist until all that is left in this field will be these scientific opium addicts, dreaming and reading one another's absurdities in a blue haze.

Comments on Solid State physics 3, p.93 (1070)

High Tc Superconductors?

Search for new SC with higher Tc mainly in metals and alloys

Oxides not considered – against the mainstream and common understanding



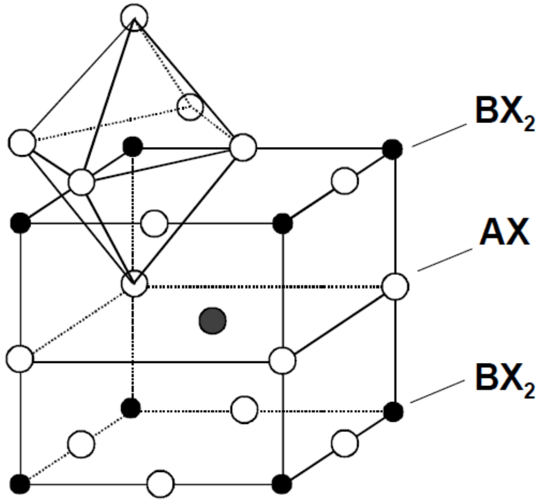
Was this the limit?

Many said yes

Oxides superconductors

Superconductivity (Tc =0,3 K) was found in 1964 in the **perovskite oxide $SrTiO_3$**

At IBM Rushlikon Laboratory in Zurich, **Gerd Binnig** (inventor of STM) in a team with **Georg Bednondz** push up Tc to 1,2 K with **Nb doping**



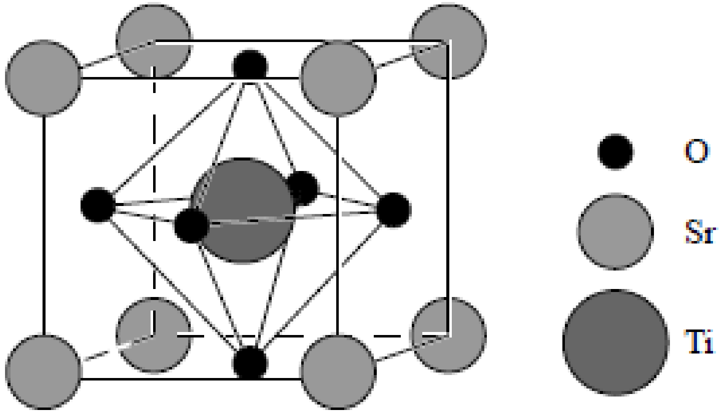


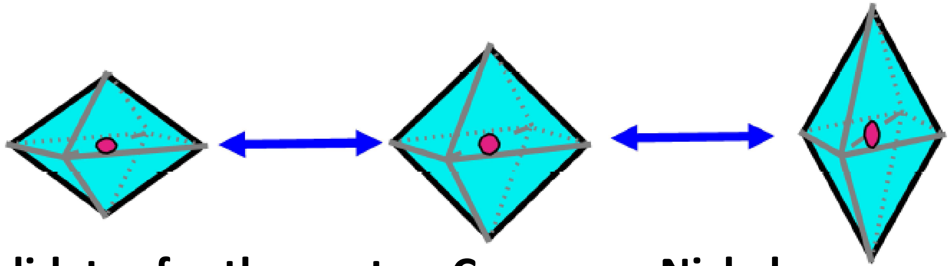
Figure 2.7 The cubic ABX_3 structure. A prominent example is $SrTiO_3$.

The discovery of cuprate superconductors

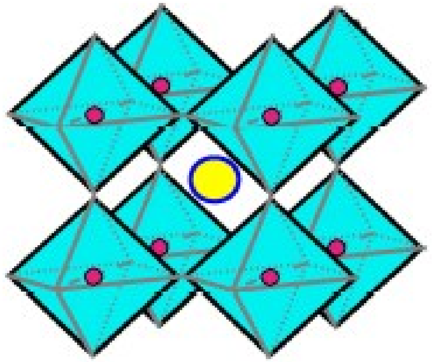
J. George Bernondz and **K. Alex Muller** (that substituted Gerd Binnig) open a new era of Superconductivity in 1986

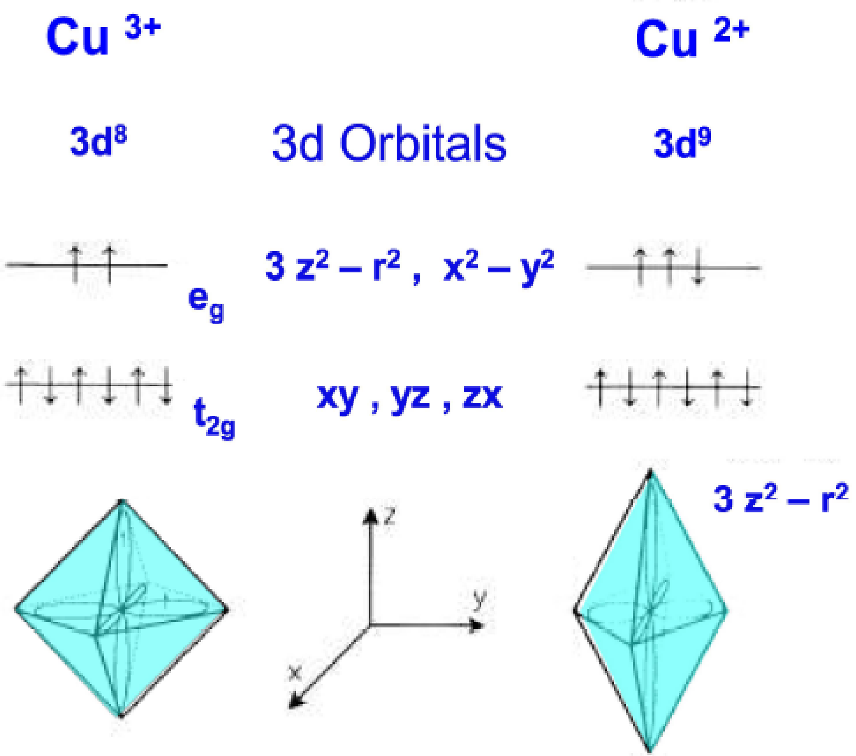
They studied materials which showed **Jahn-Teller effect**

Electron Transfer causes dynamic JT effect → LATTICE VIBRATIONS



Candidates for the center: Copper or Nickel



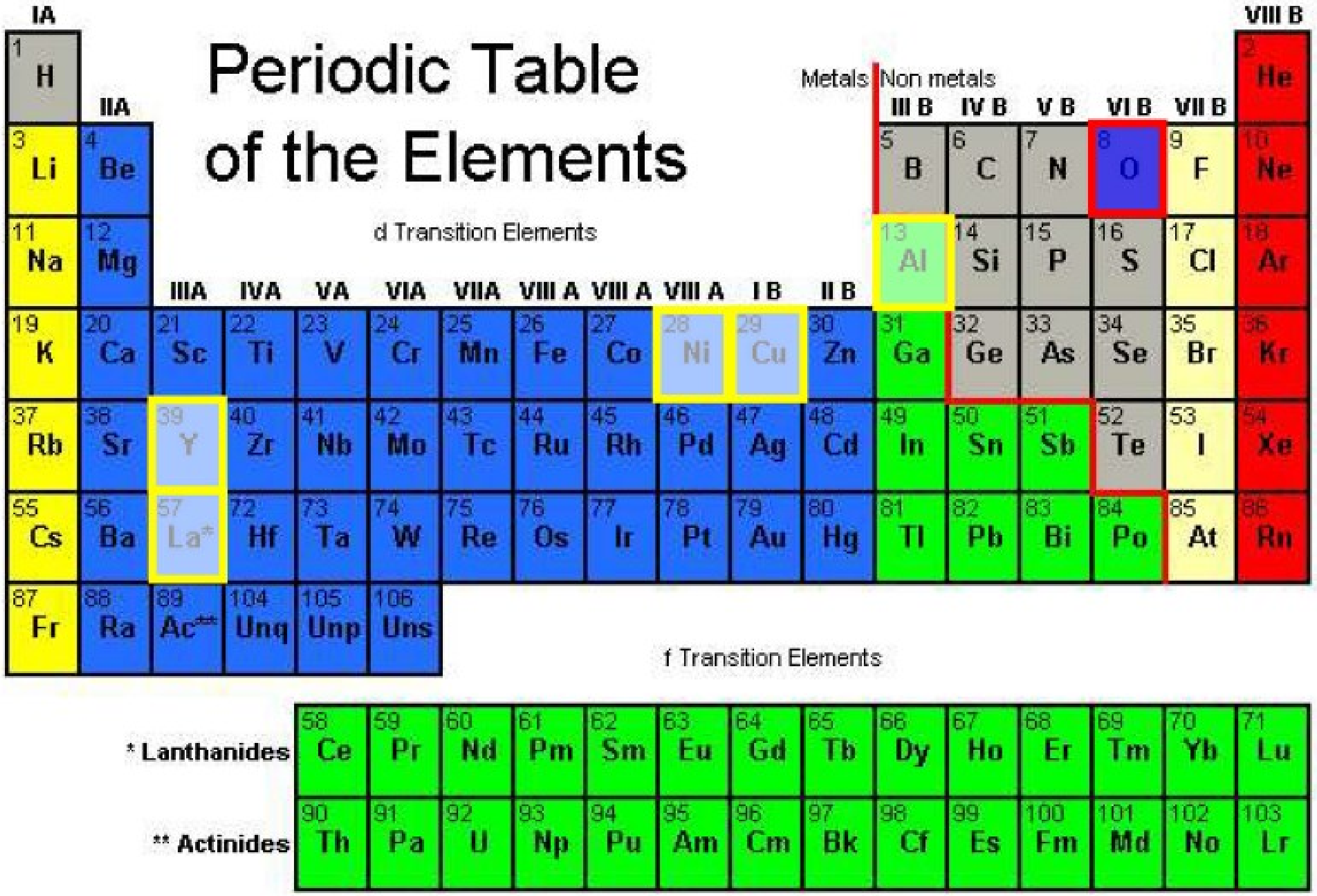


Jahn-Teller Effect
Elongation
of Octahedron

J. Georg Bednorz – From LS to HTS, EASITrain School in Wien, 2019

1983

The discovery of cuprate superconductors



Periodic Table of the Elements

d Transition Elements

Metals | Non metals

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII A	VIII A	VIII A	I B	II B	III B	IV B	V B	VI B	VII B	VIII B
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 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac**	104 Unq	105 Unp	106 Uns												

f Transition Elements

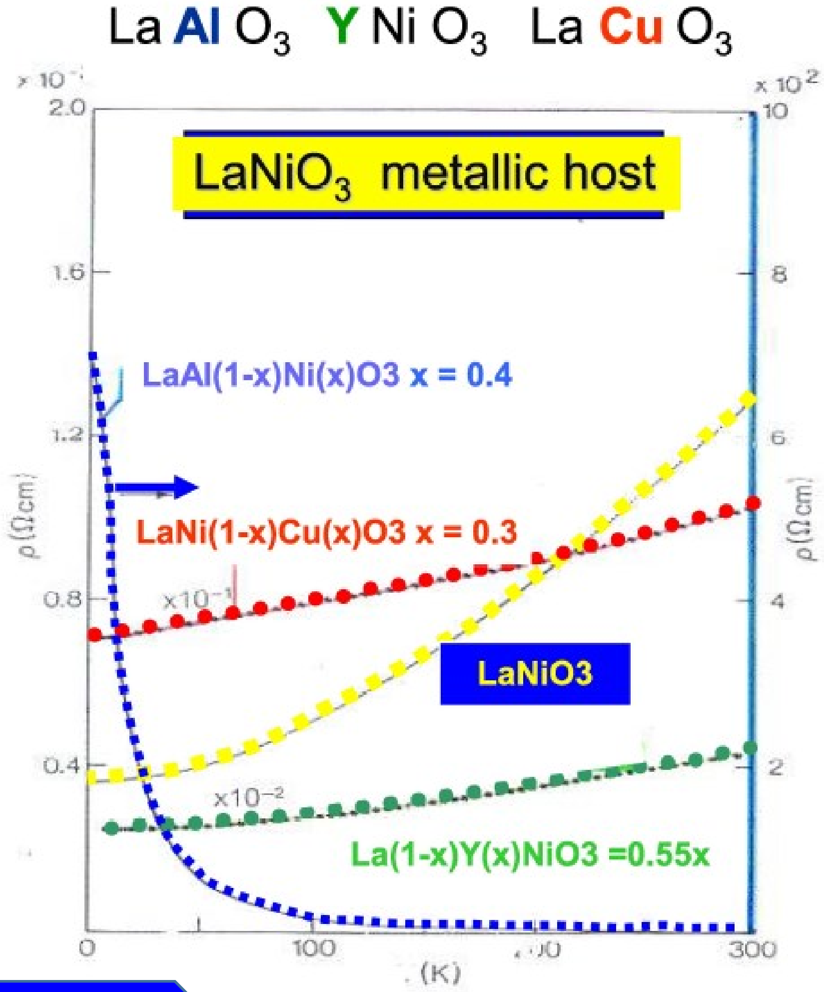
* Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

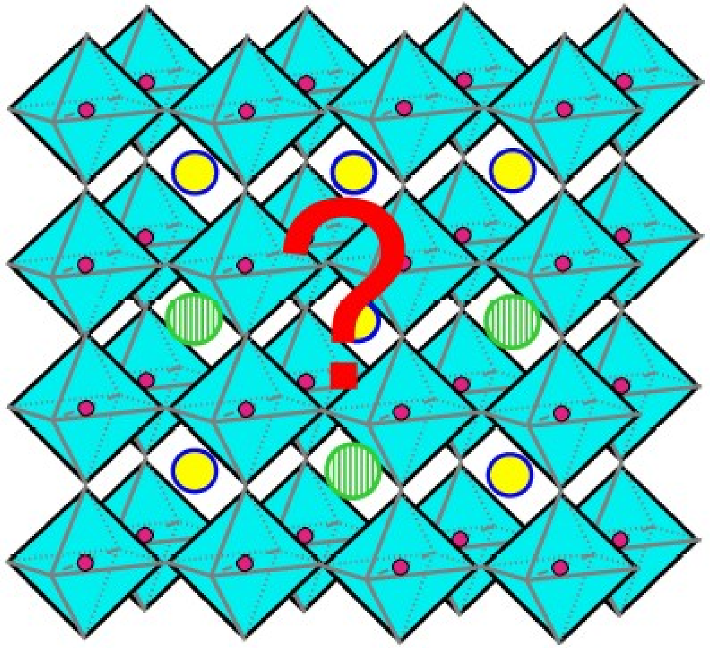
Combination with six Elements only- still many possibilities

1983

J. Georg Bednorz – From LS to HTS, EASITrain School in Wien, 2019

The discovery of cuprate superconductors





3 Years Later no encouraging signs…

1983

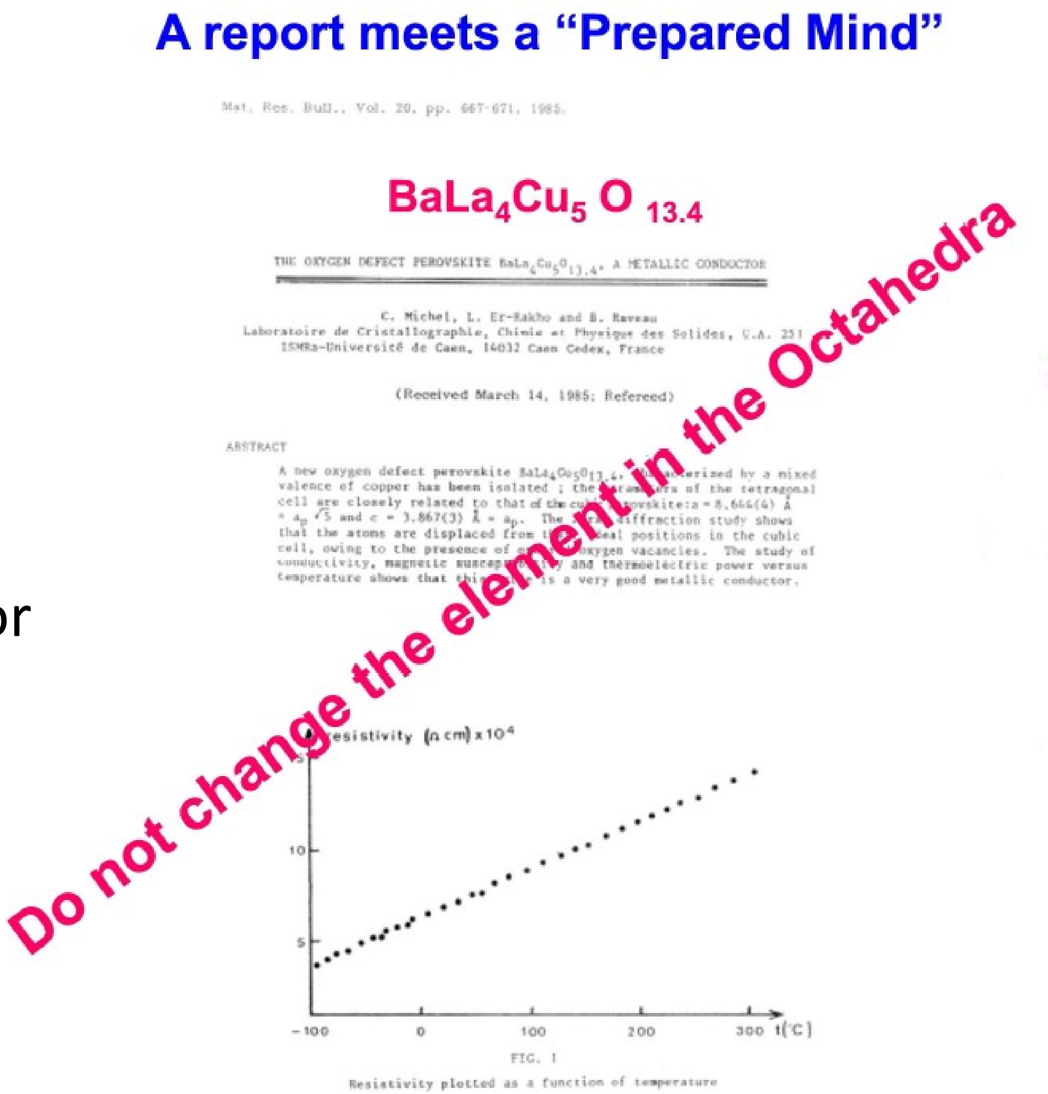
1985

J. Georg Bednorz – From LS to HTS, EASITrain School in Wien, 2019

The discovery of cuprate superconductors

A French group reported in 1985 **metallic behaviour between 300°C and -100 °C in a perovskite containing barium, lanthanum, copper and oxygen**

Bernodz and Muller understood the potential of the structure as Superconductor



A report meets a "Prepared Mind"

Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.

$BaLa_4Cu_5O_{13.4}$

THE OXYGEN DEFECT PEROVSKITE $BaLa_4Cu_5O_{13.4}$, A METALLIC CONDUCTOR

C. Michel, L. Er-Rakho and B. Raveau
Laboratoire de Cristallographie, Chimie et Physique des Solides, U.A. 251
ISMRa-Université de Caen, 14032 Caen Cedex, France

(Received March 14, 1985; Refereed)

ABSTRACT

A new oxygen defect perovskite $BaLa_4Cu_5O_{13.4}$, characterized by a mixed valence of copper has been isolated ; the parameters of the tetragonal cell are closely related to that of the cubic perovskite: $a = 8.644(4)$ Å $= a_p\sqrt{5}$ and $c = 3.867(3)$ Å $= a_p$. The [illegible] diffraction study shows that the atoms are displaced from [illegible] ideal positions in the cubic cell, owing to the presence of [illegible] oxygen vacancies. The study of conductivity, magnetic susceptibility and thermoelectric power versus temperature shows that [illegible] is a very good metallic conductor.

FIG. 1

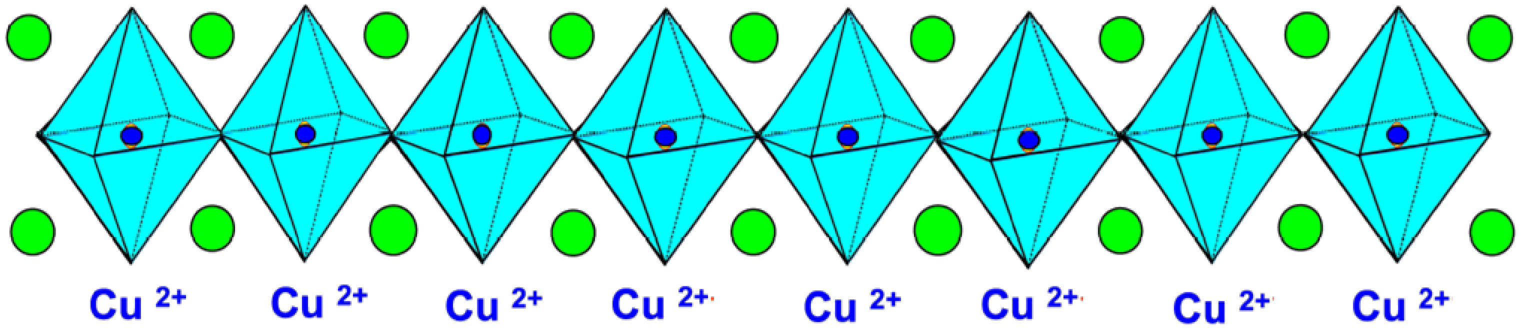
Resistivity plotted as a function of temperature

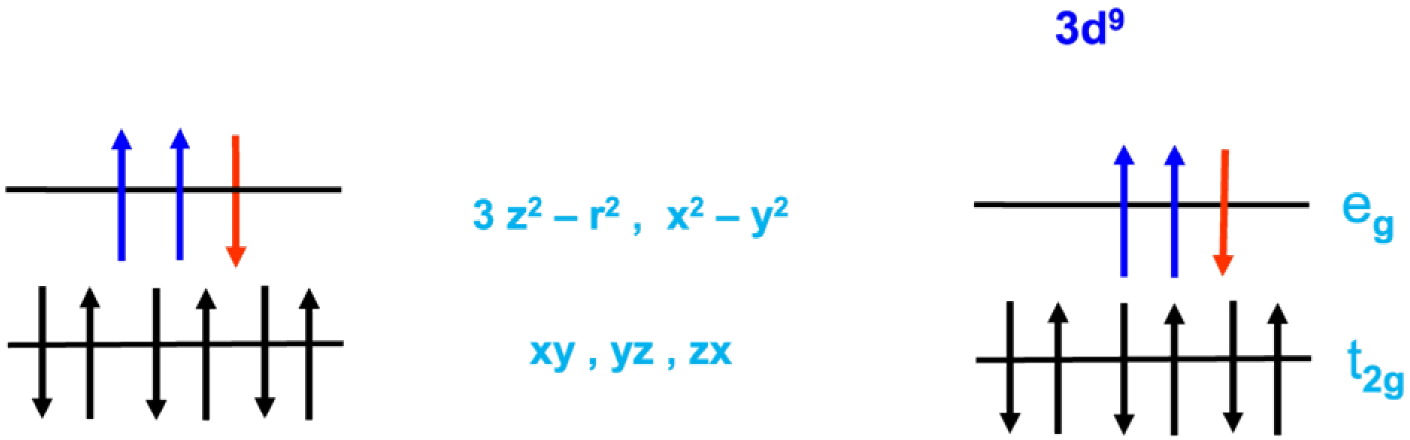
J. Georg Bednorz – From LS to HTS, EASITrain School in Wien, 2019

1983

1985

The discovery of cuprate superconductors



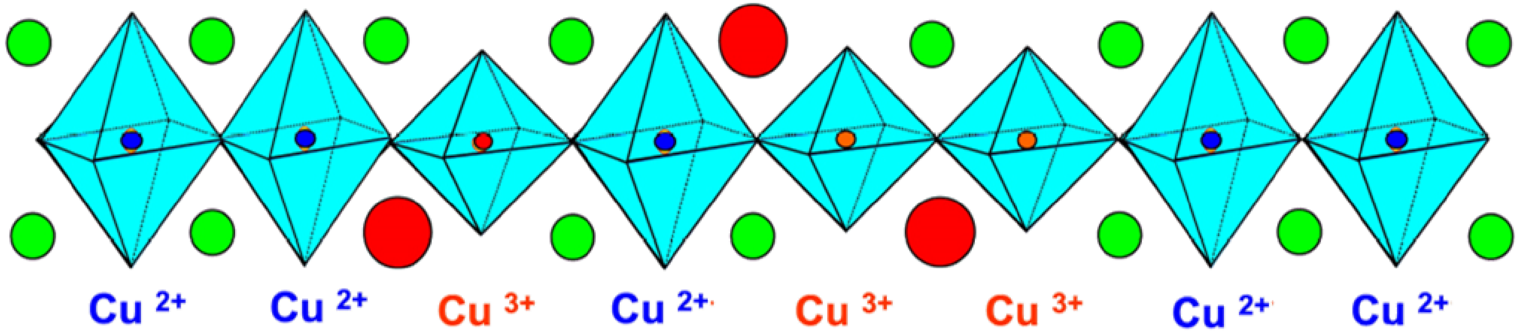


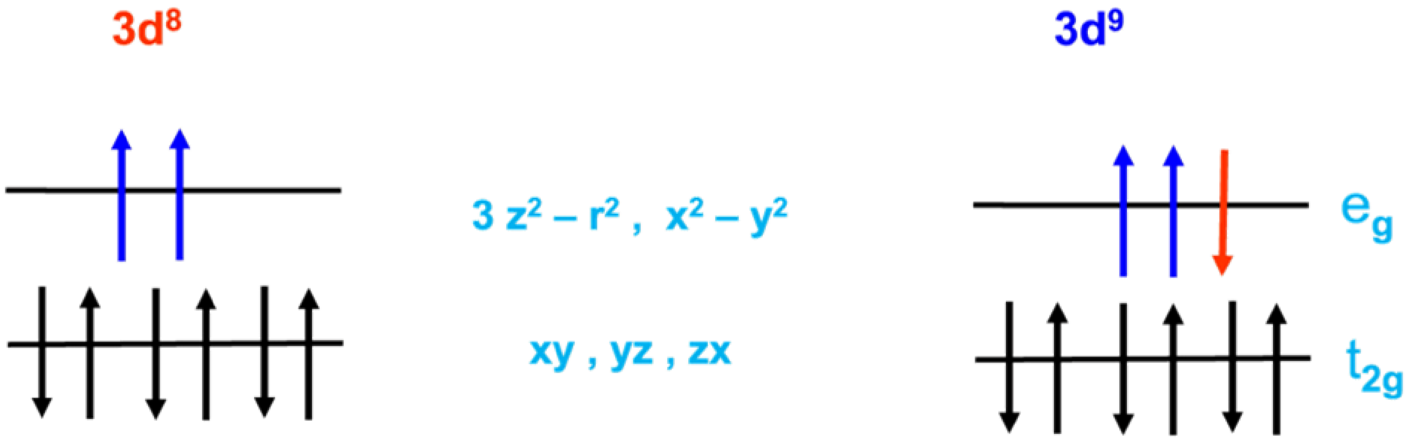
Creation of Charge Carriers by Ionic Substitution

Local Chemical Variation - Spontaneous Distortion Jahn - Teller effect

J. Georg Bednorz – From LS to HTS, EASITrain School in Wien, 2019

The discovery of cuprate superconductors





Creation of Charge Carriers by Ionic Substitution

Local Chemical Variation - Spontaneous Distortion Jahn - Teller effect

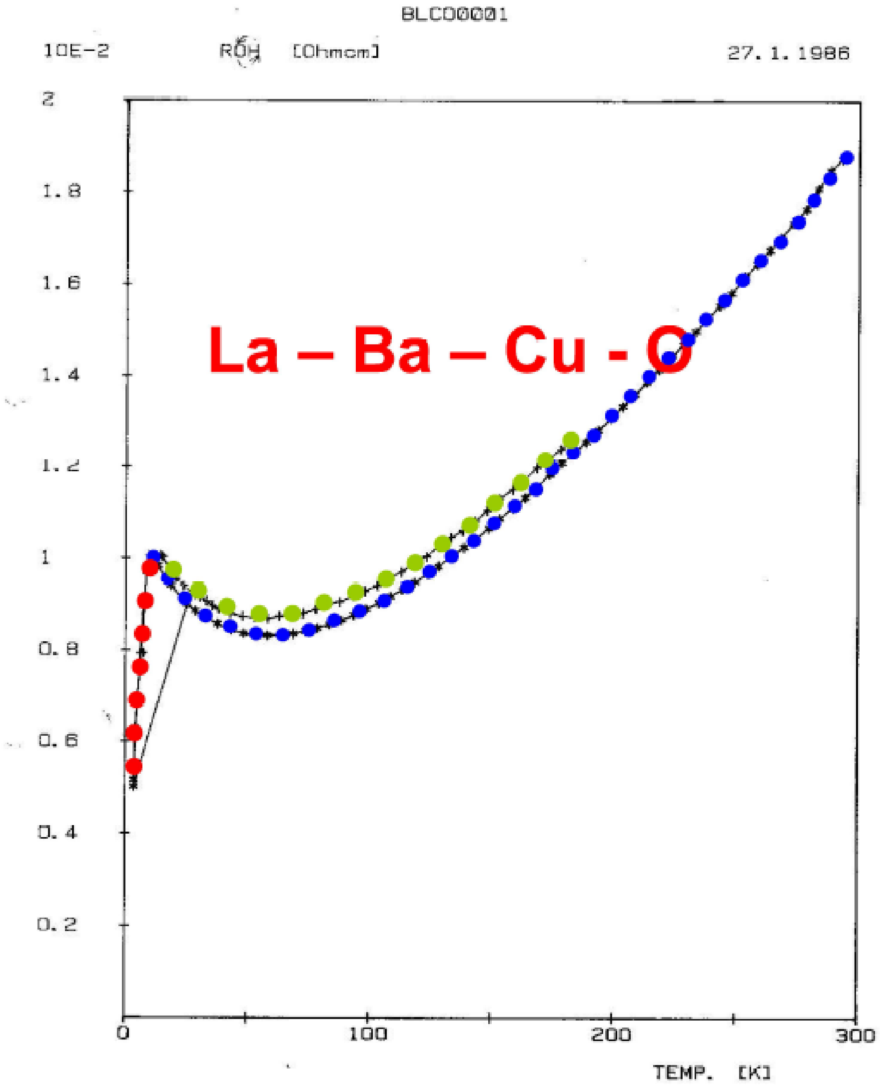
1983

1985

J. Georg Bednorz – From LS to HTS, EASITrain School in Wien, 2019

The discovery of cuprate superconductors

First sign of a Superconductor…



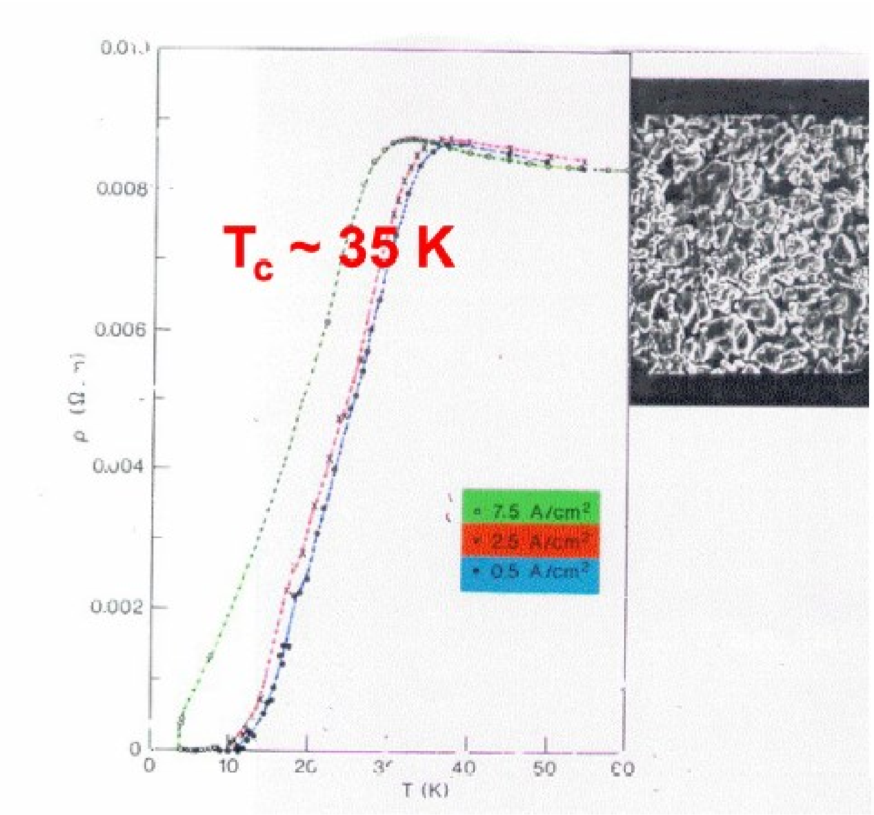
J. Georg Bednorz – From LS to HTS, EASITrain School in Wien, 2019

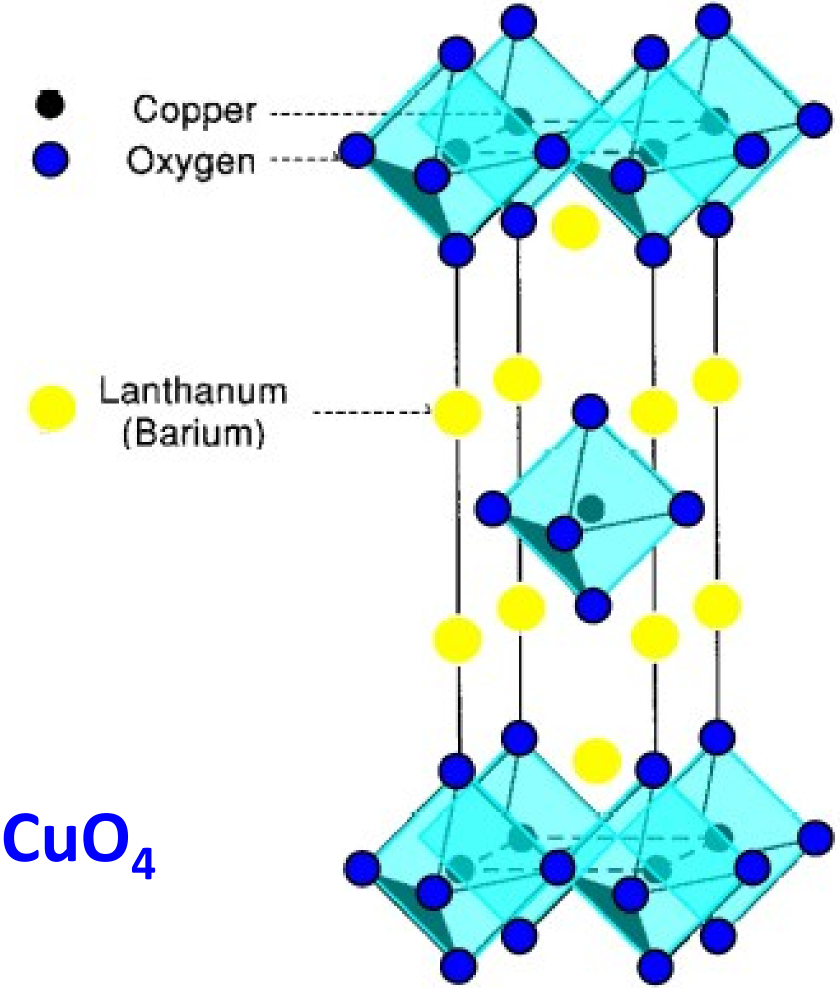
1983

1985

January 1986

The discovery of cuprate superconductors





Bernodz and Muller get Tc of 30 K in $La_{2-x}Ba_xCuO_4$

1983

1985

January 1986

April 1986

J. Georg Bednorz – From LS to HTS, EASITrain School in Wien, 2019

The discovery of cuprate superconductors

- The work was published on Zeitschrift fur Physik to avoid refereeing process
- At first, a shy reception from the scientific community

1983 | 1985 | January 1986 | April 1986 | **August 1986**

The discovery of cuprate superconductors

- The work was published on Zeitschrift fur Physik to avoid refereeing process
- At first, a shy reception from the scientific community
- At Houston, Paul Chu (student of Bernd Mathias in San Diego) read the paper
- Duplicate the work and applying a **pressure of 13 kBar push Tc from 30K to 40K**

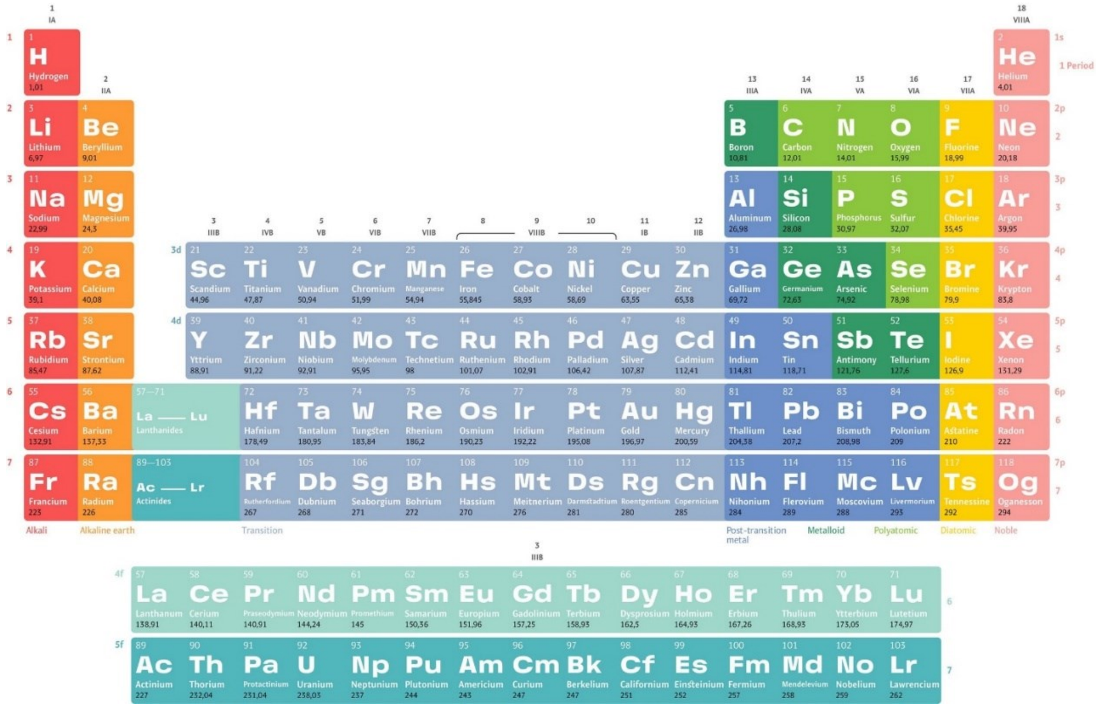
1983 | 1985 | January 1986 | April 1986 | August 1986 | **November 1986**

The discovery of cuprate superconductors

- The work was published on Zeitschrift fur Physik to avoid refereeing process
- At first, a shy reception from the scientific community
- At Houston, Paul Chu (student of Bernd Mathias in San Diego) read the paper
- Duplicate the work and applying a **pressure of 13 kBar pusch Tc from 30K to 40K**
- Chu announced the result at a Conference
- Koichi Kitazawa of the University of Tokyo also duplicated the Zurich work and in addition identified the composition of the superconducting part

1983 | 1985 | January 1986 | April 1986 | August 1986 | November 1986 | December 1986

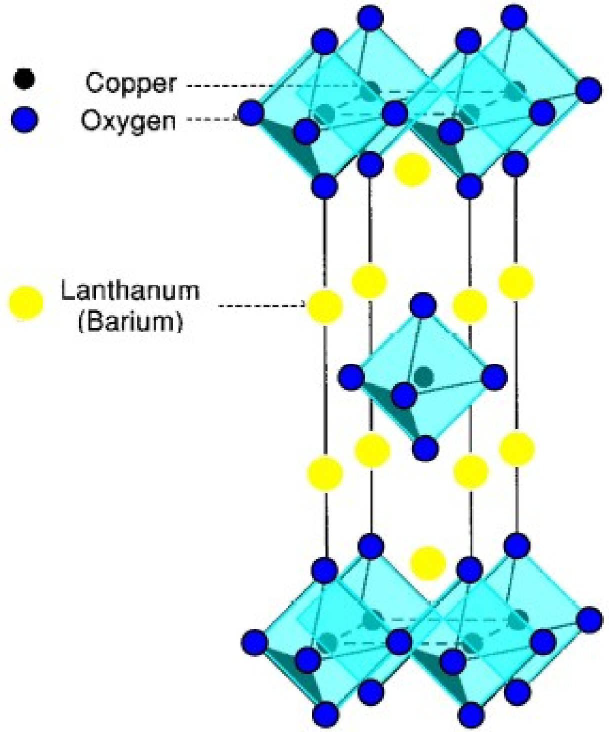
How to increase Tc in cuprates?



	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA	
1	1 H Hydrogen 1,01																	2 He Helium 4,01	1s 1 Period
2	3 Li Lithium 6,97	4 Be Beryllium 9,01											5 B Boron 10,81	6 C Carbon 12,01	7 N Nitrogen 14,01	8 O Oxygen 15,99	9 F Fluorine 18,99	10 Ne Neon 20,18	2p 2
3	11 Na Sodium 22,99	12 Mg Magnesium 24,3											13 Al Aluminum 26,98	14 Si Silicon 28,08	15 P Phosphorus 30,97	16 S Sulfur 32,07	17 Cl Chlorine 35,45	18 Ar Argon 39,95	3p 3
4 3d	19 K Potassium 39,1	20 Ca Calcium 40,08	21 Sc Scandium 44,96	22 Ti Titanium 47,87	23 V Vanadium 50,94	24 Cr Chromium 51,99	25 Mn Manganese 54,94	26 Fe Iron 55,845	27 Co Cobalt 58,93	28 Ni Nickel 58,69	29 Cu Copper 63,55	30 Zn Zinc 65,38	31 Ga Gallium 69,72	32 Ge Germanium 72,63	33 As Arsenic 74,92	34 Se Selenium 78,98	35 Br Bromine 79,9	36 Kr Krypton 83,8	4p 4
5 4d	37 Rb Rubidium 85,47	38 Sr Strontium 87,62	39 Y Yttrium 88,91	40 Zr Zirconium 91,22	41 Nb Niobium 92,91	42 Mo Molybdenum 95,95	43 Tc Technetium 98	44 Ru Ruthenium 101,07	45 Rh Rhodium 102,91	46 Pd Palladium 106,42	47 Ag Silver 107,87	48 Cd Cadmium 112,41	49 In Indium 114,81	50 Sn Tin 118,71	51 Sb Antimony 121,76	52 Te Tellurium 127,6	53 I Iodine 126,9	54 Xe Xenon 131,29	5p 5
6	55 Cs Cesium 132,91	56 Ba Barium 137,33	57—71 La —— Lu Lanthanides	72 Hf Hafnium 178,49	73 Ta Tantalum 180,95	74 W Tungsten 183,84	75 Re Rhenium 186,2	76 Os Osmium 190,23	77 Ir Iridium 192,22	78 Pt Platinum 195,08	79 Au Gold 196,97	80 Hg Mercury 200,59	81 Tl Thallium 204,38	82 Pb Lead 207,2	83 Bi Bismuth 208,98	84 Po Polonium 209	85 At Astatine 210	86 Rn Radon 222	6p 6
7	87 Fr Francium 223	88 Ra Radium 226	89—103 Ac —— Lr Actinides	104 Rf Rutherfordium 267	105 Db Dubnium 268	106 Sg Seaborgium 271	107 Bh Bohrium 272	108 Hs Hassium 270	109 Mt Meitnerium 276	110 Ds Darmstadtium 281	111 Rg Roentgentium 280	112 Cn Copernicium 285	113 Nh Nihonium 284	114 Fl Flerovium 289	115 Mc Moscovium 288	116 Lv Livermorium 293	117 Ts Tennessine 292	118 Og Oganesson 294	7p 7
	Alkali	Alkaline earth		Transition									Post-transition metal	Metalloid	Polyatomic		Diatomic	Noble	

3
IIIB

4f	57 La Lanthanum 138,91	58 Ce Cerium 140,11	59 Pr Praseodymium 140,91	60 Nd Neodymium 144,24	61 Pm Promethium 145	62 Sm Samarium 150,36	63 Eu Europium 151,96	64 Gd Gadolinium 157,25	65 Tb Terbium 158,93	66 Dy Dysprosium 162,5	67 Ho Holmium 164,93	68 Er Erbium 167,26	69 Tm Thulium 168,93	70 Yb Ytterbium 173,05	71 Lu Lutetium 174,97	6
5f	89 Ac Actinium 227	90 Th Thorium 232,04	91 Pa Protactinium 231,04	92 U Uranium 238,03	93 Np Neptunium 237	94 Pu Plutonium 244	95 Am Americium 243	96 Cm Curium 247	97 Bk Berkelium 247	98 Cf Californium 251	99 Es Einsteinium 252	100 Fm Fermium 257	101 Md Mendelevium 258	102 No Nobelium 259	103 Lr Lawrencium 262	7



1983

1985

January 1986

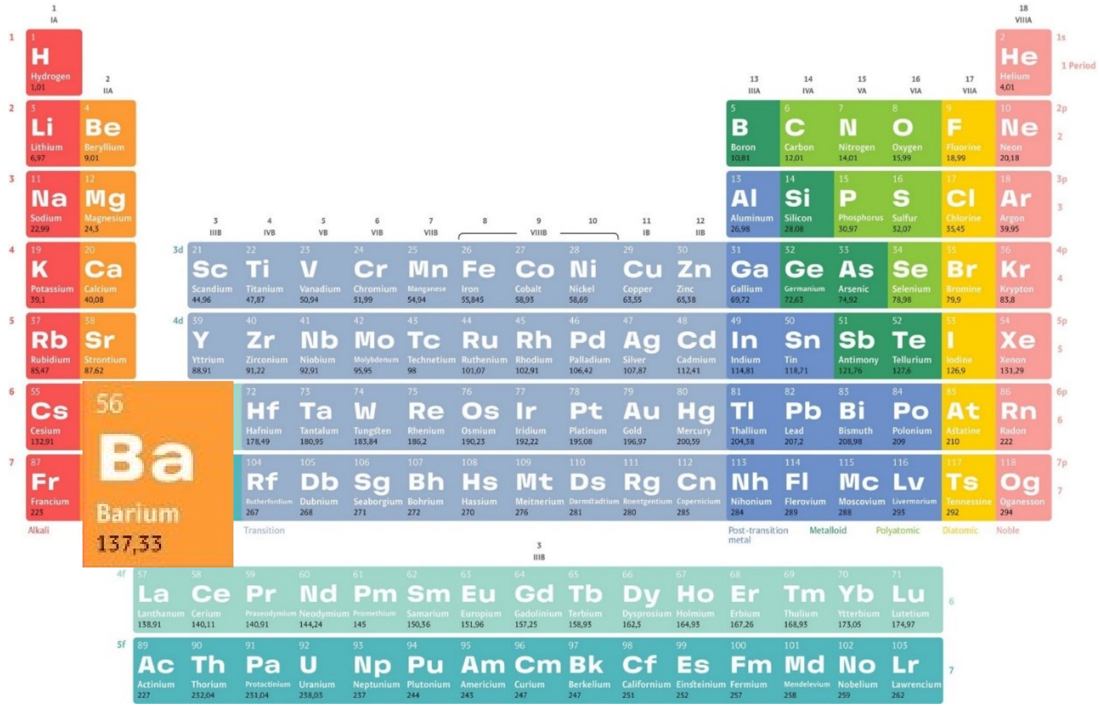
April 1986

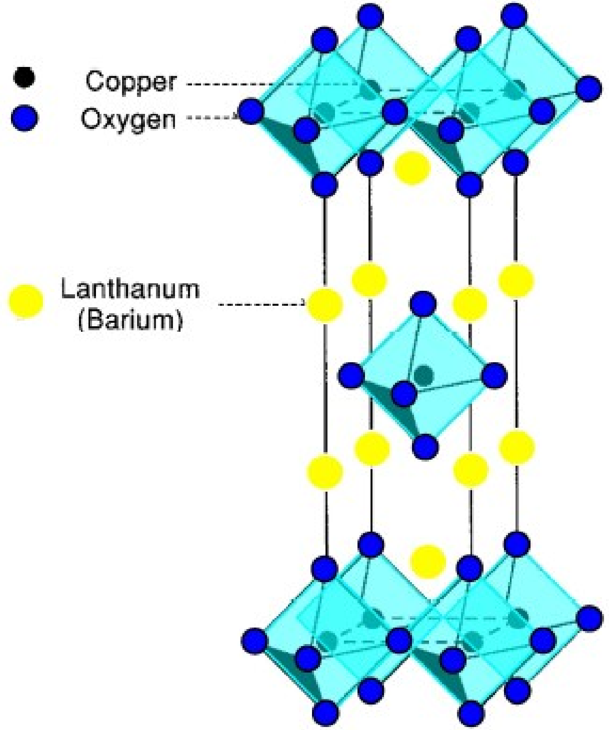
August 1986

November 1986

December 1986

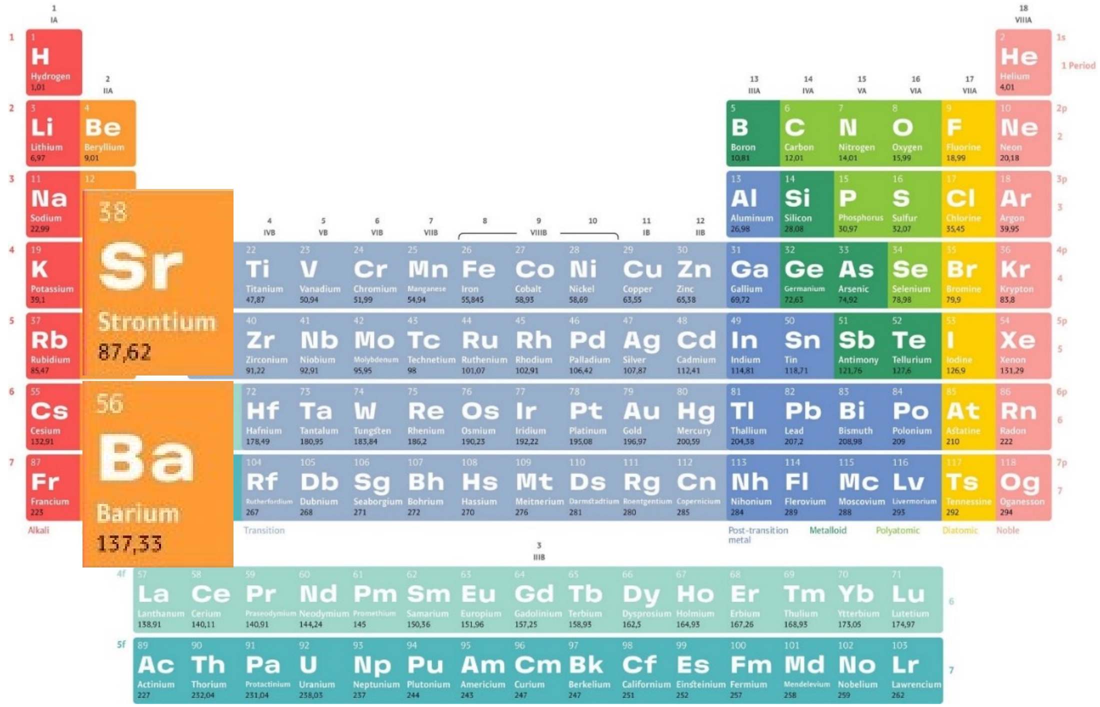
How to increase Tc in cuprates?

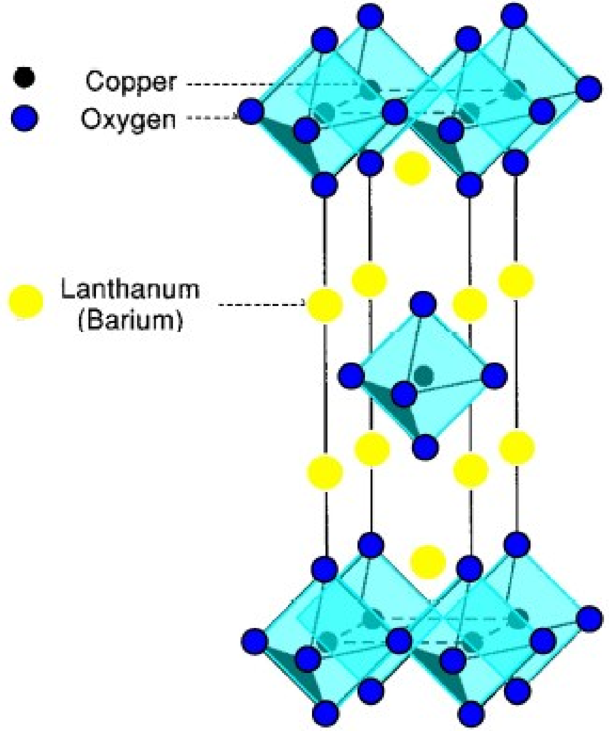




1983 | 1985 | January 1986 | April 1986 | August 1986 | November 1986 | **December 1986**

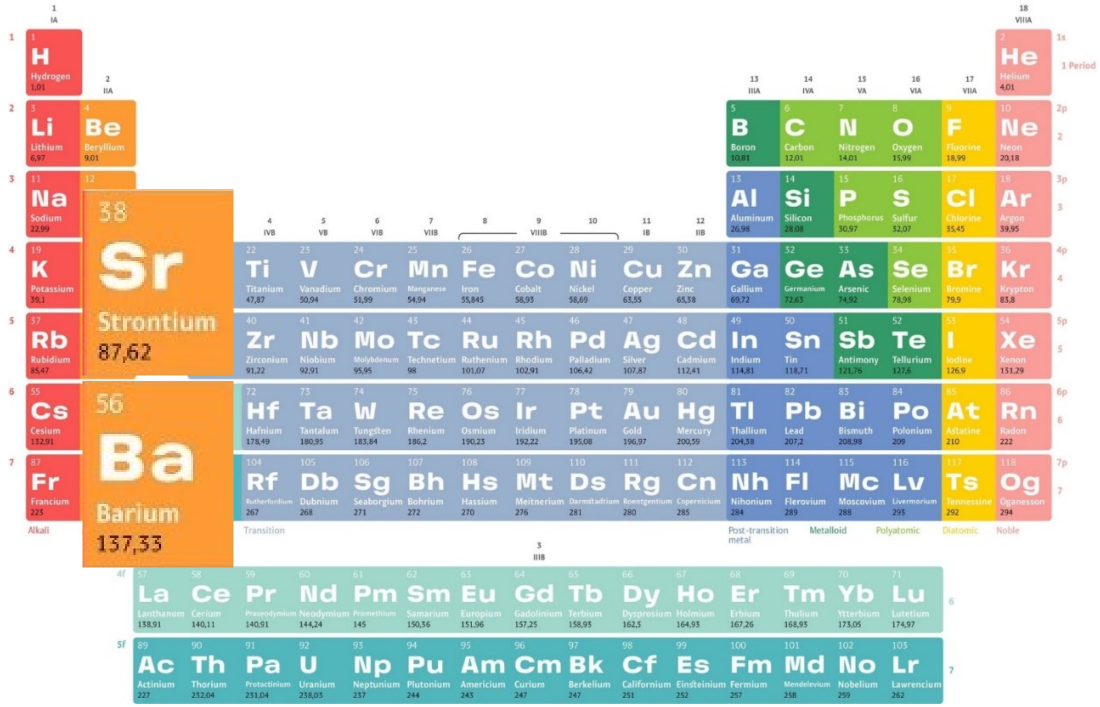
How to increase Tc in cuprates?

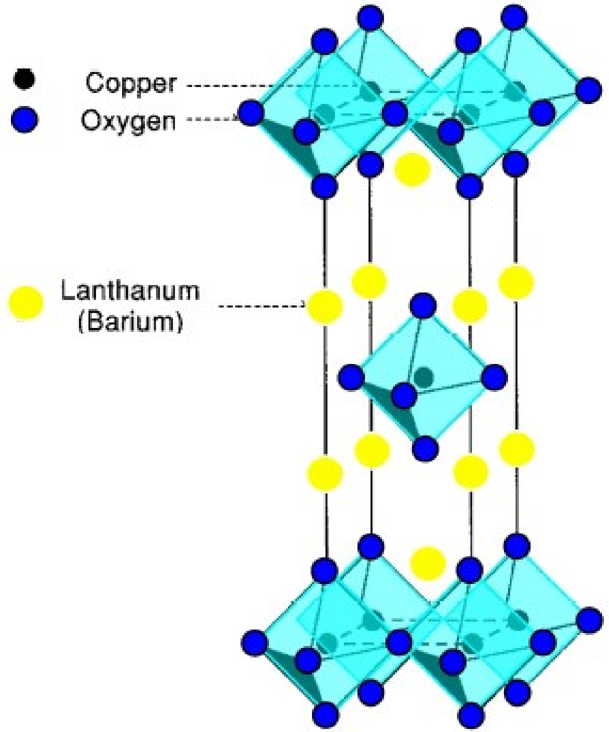




1983 | 1985 | January 1986 | April 1986 | August 1986 | November 1986 | **December 1986**

How to increase Tc in cuprates?



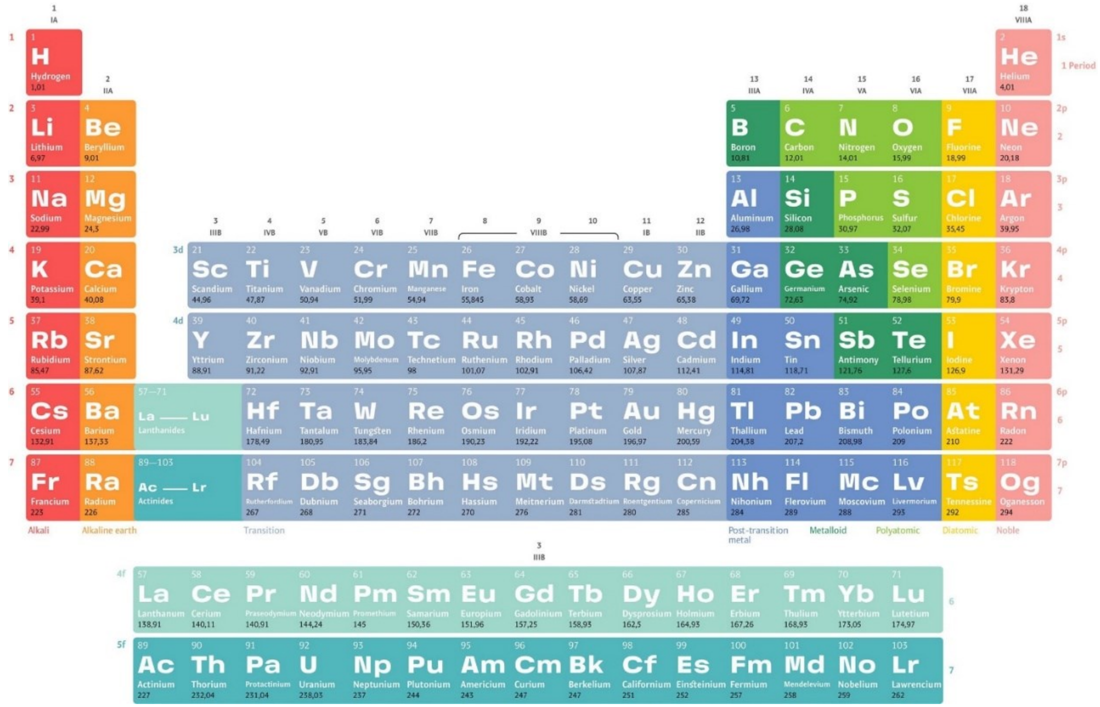


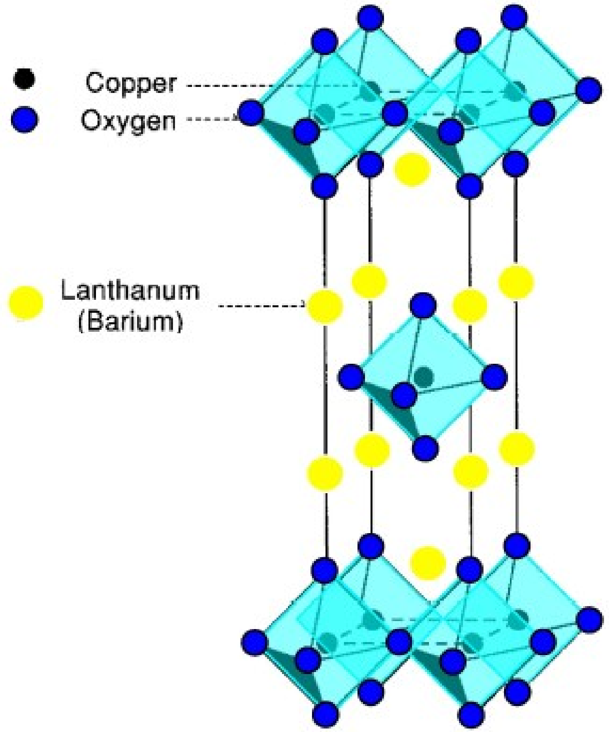
Chu **replace Ba with Sr** obtaining the same effect of the pressure (Tc 39 K)

At Bell Labs Sr compound showed Tc=36 K and **Meissner effect was proved**

1983
1985
January 1986
April 1986
August 1986
November 1986
December 1986

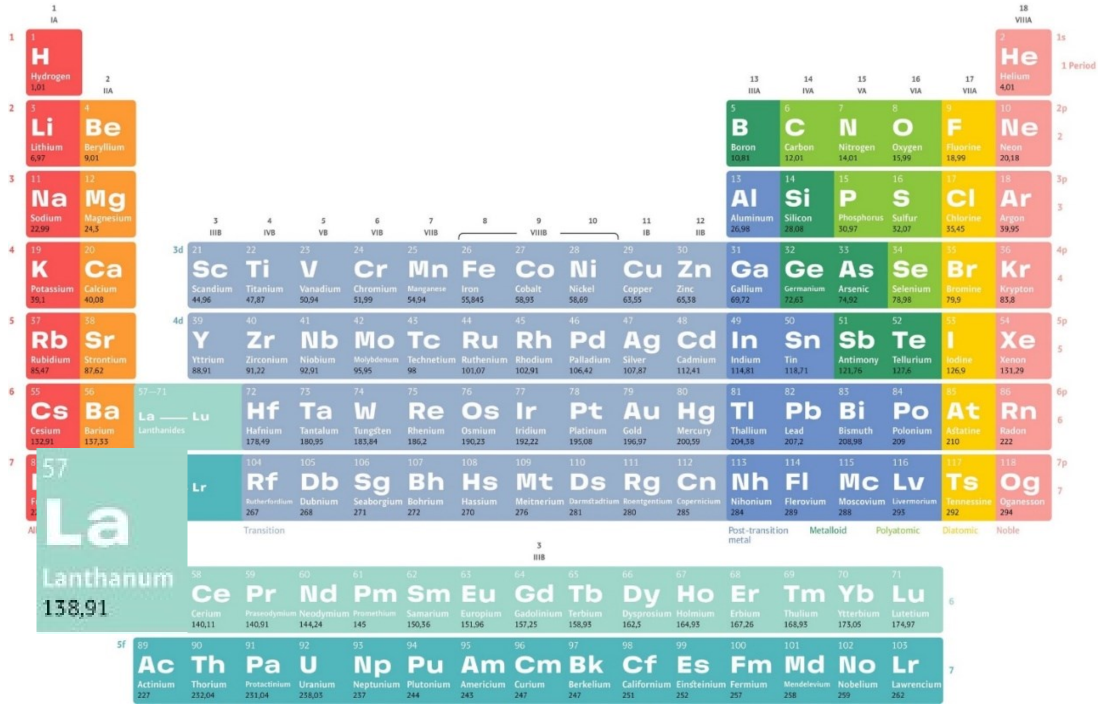
How to increase Tc in cuprates?

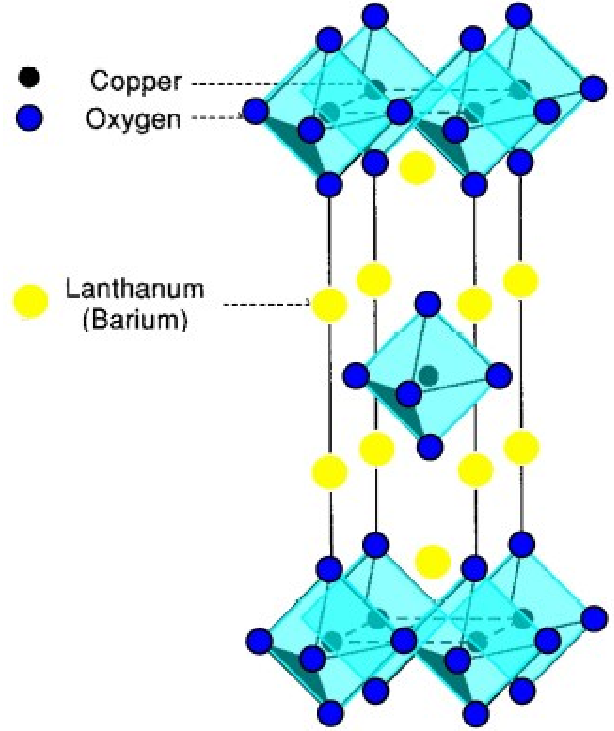




1983 | 1985 | January 1986 | April 1986 | August 1986 | November 1986 | December 1986 | **January 1987**

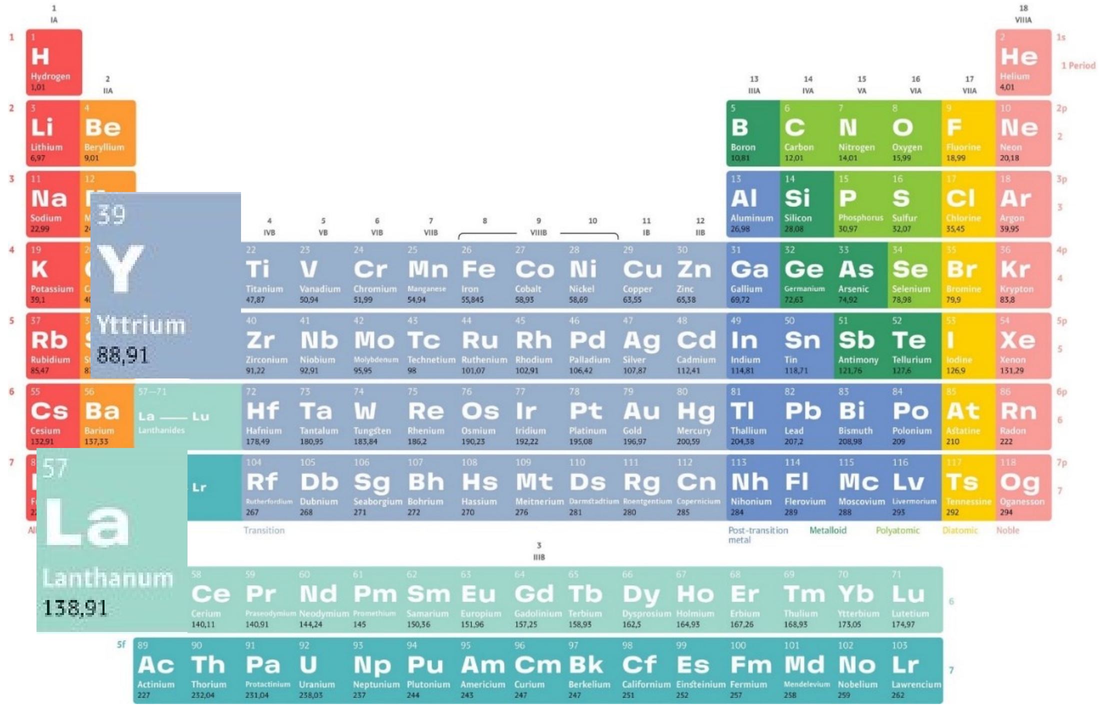
How to increase Tc in cuprates?





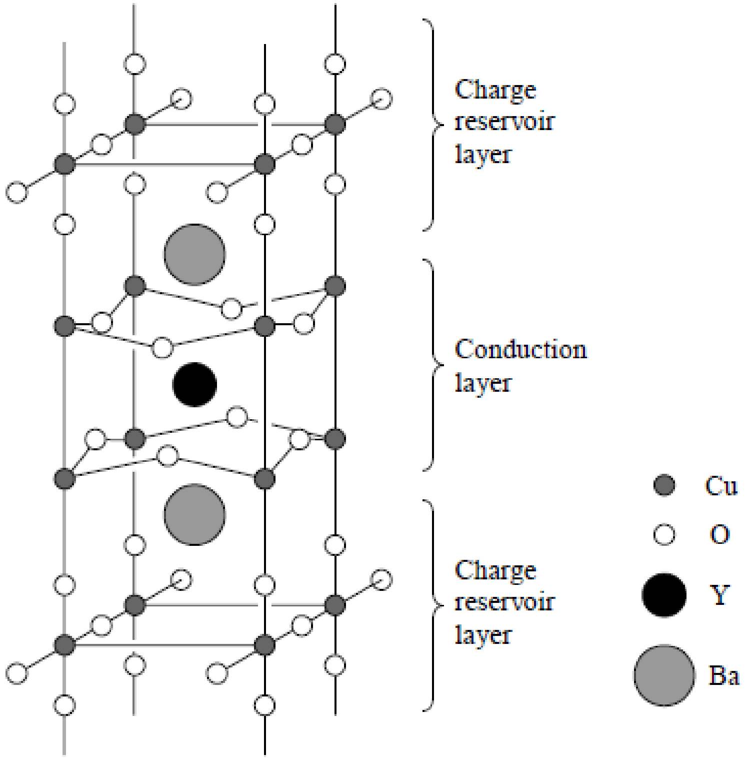
1983 | 1985 | January 1986 | April 1986 | August 1986 | November 1986 | December 1986 | **January 1987**

How to increase Tc in cuprates?



Chu **replace La with Y** obtaining a **Tc of 93 K!!!**

Higher than Nitrogen boiling point (77 K)



Structure of orthorhombic $YBa_2Cu_3O_7$ aka YBCO

1983 | 1985 | January 1986 | April 1986 | August 1986 | November 1986 | December 1986 | **January 1987**

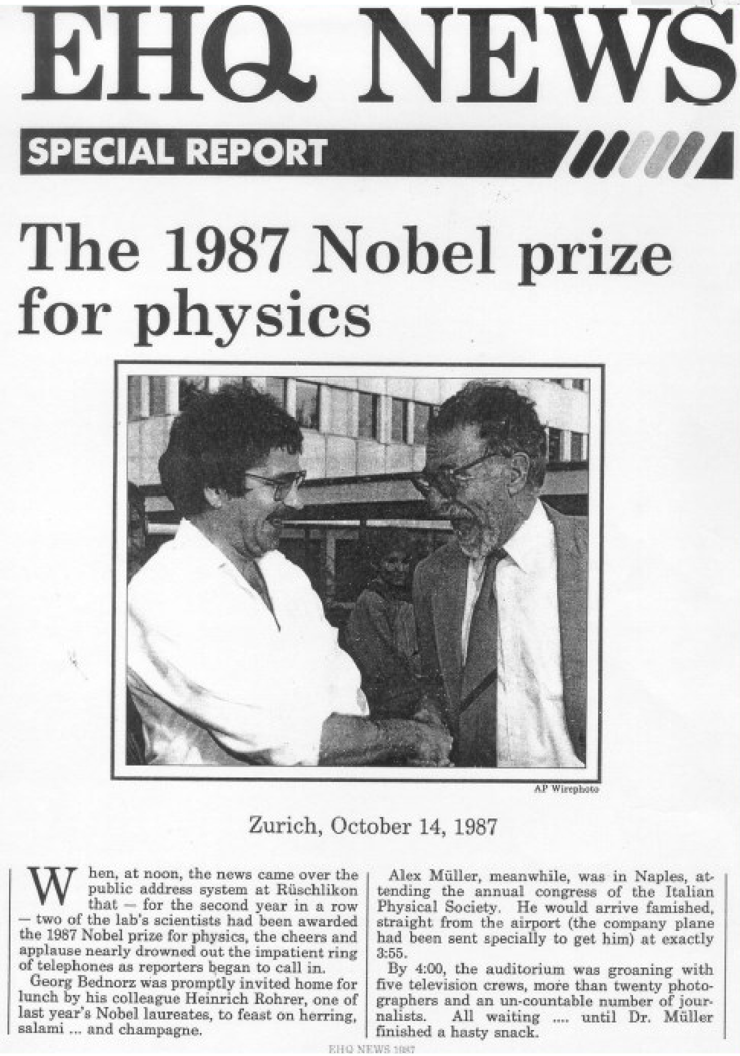
How to publish without the risk of copy

- **The syntesis of YBCO is relatively easy** (shake and bake)
- Chu was faced with the same dilemma of Bednorz and Muller: where to publish the results?
- Chu asked to Physical Review Letters to publish without review
- He obtained «only» to choose the reviewer
- Chu substitute in the manuscript Y with Yb and correct the paper just before the publication
- Can you imagine the reaction of scientific comunity?

New era of Superconductivity

30. The Woodstock of physics

The American Physical Society Meeting (March 1987)



EHQ NEWS

SPECIAL REPORT

The 1987 Nobel prize for physics

AP Wirephoto

Zurich, October 14, 1987

When, at noon, the news came over the public address system at Rüschlikon that — for the second year in a row — two of the lab's scientists had been awarded the 1987 Nobel prize for physics, the cheers and applause nearly drowned out the impatient ring of telephones as reporters began to call in.

Georg Bednorz was promptly invited home for lunch by his colleague Heinrich Rohrer, one of last year's Nobel laureates, to feast on herring, salami ... and champagne.

Alex Müller, meanwhile, was in Naples, attending the annual congress of the Italian Physical Society. He would arrive famished, straight from the airport (the company plane had been sent specially to get him) at exactly 3:55.

By 4:00, the auditorium was groaning with five television crews, more than twenty photographers and an un-countable number of journalists. All waiting .... until Dr. Müller finished a hasty snack.

EHQ NEWS 1987

HQ.M → R.H.M

SUPERCONDUCTORS

THE SUPERCONDUCTOR RACE HEATS UP

NATIONAL HERALD TRIBUNE, FRIDAY, JANUARY 2, 1987

Wide Use Seen for New Superconductor

By Walter Sullivan

Scientists Break Barrier For Superconductivity

By Walter Sullivan

A18

olg der Supraleitfähigkeit?

Nutzen für den Einsatz elektrischer Energie

Team Reports Breakthrough In Conductivity of Electricity

By WALTER SULLIVAN

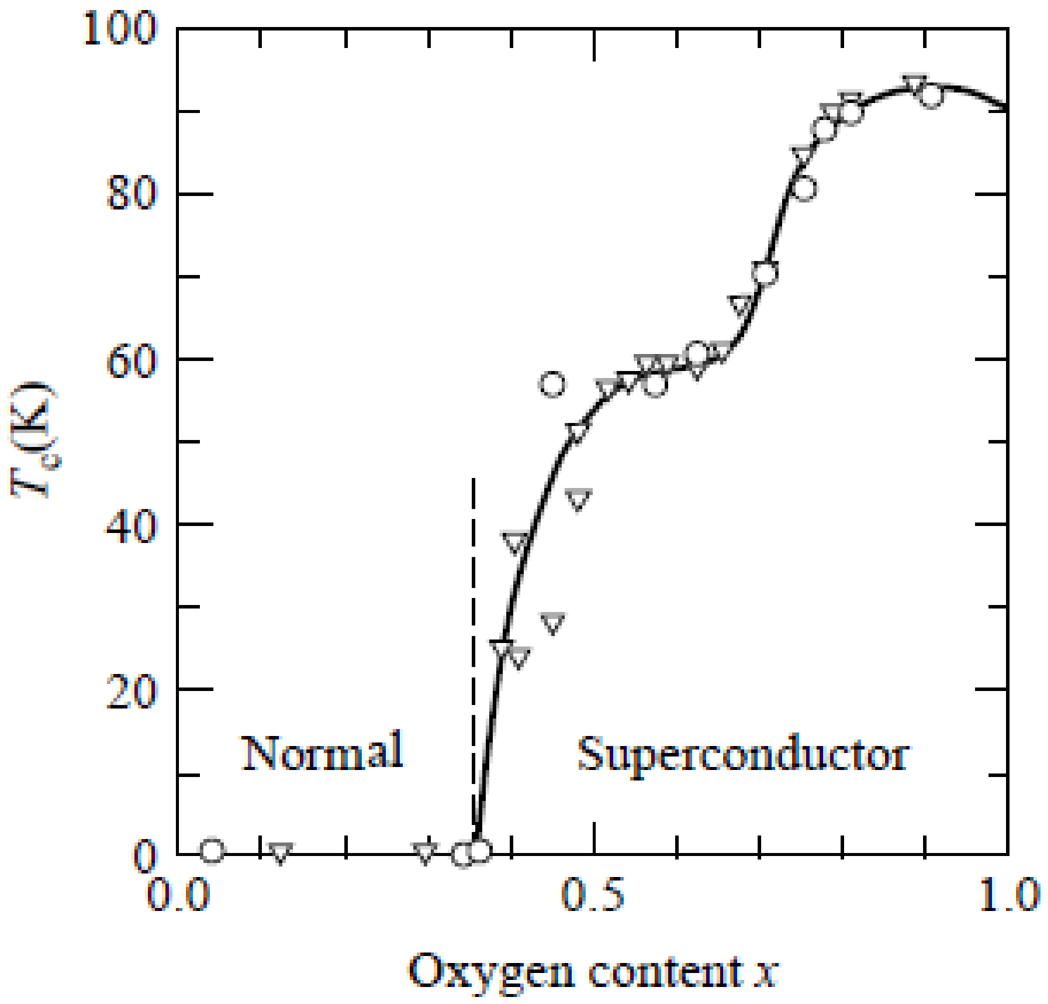
N.Y. TIMES FEB 16 1987

Révolution dans la supraconductibilité

Découverte suisse testée

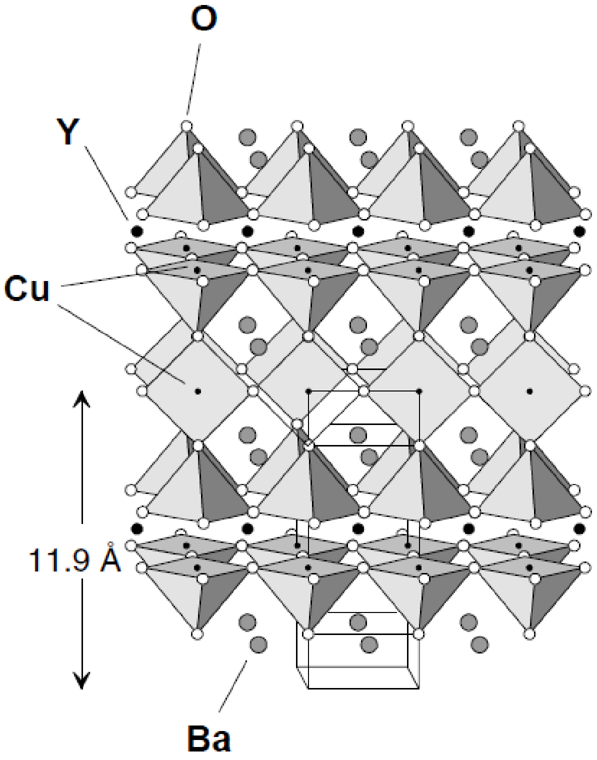
YBCO

Tc depends on Oxygen content

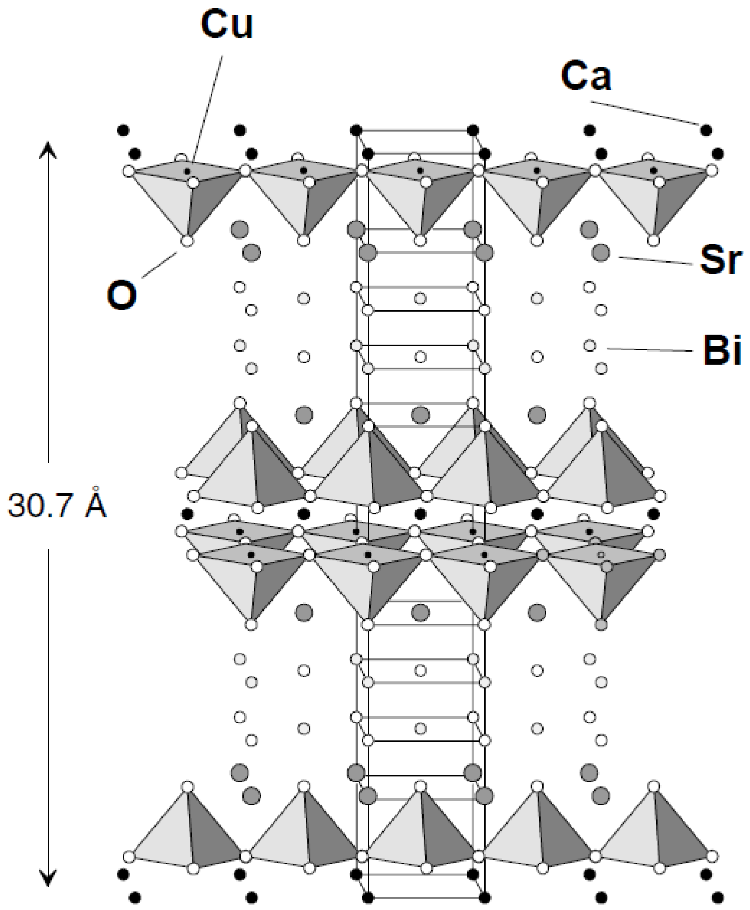


T_c versus x in $YBa_2Cu_3O_{6+x}$. Data from Cava *et al*. (circles) and from Jorgensen *et al*. (triangles)

Another importat cuprate: BSCCO

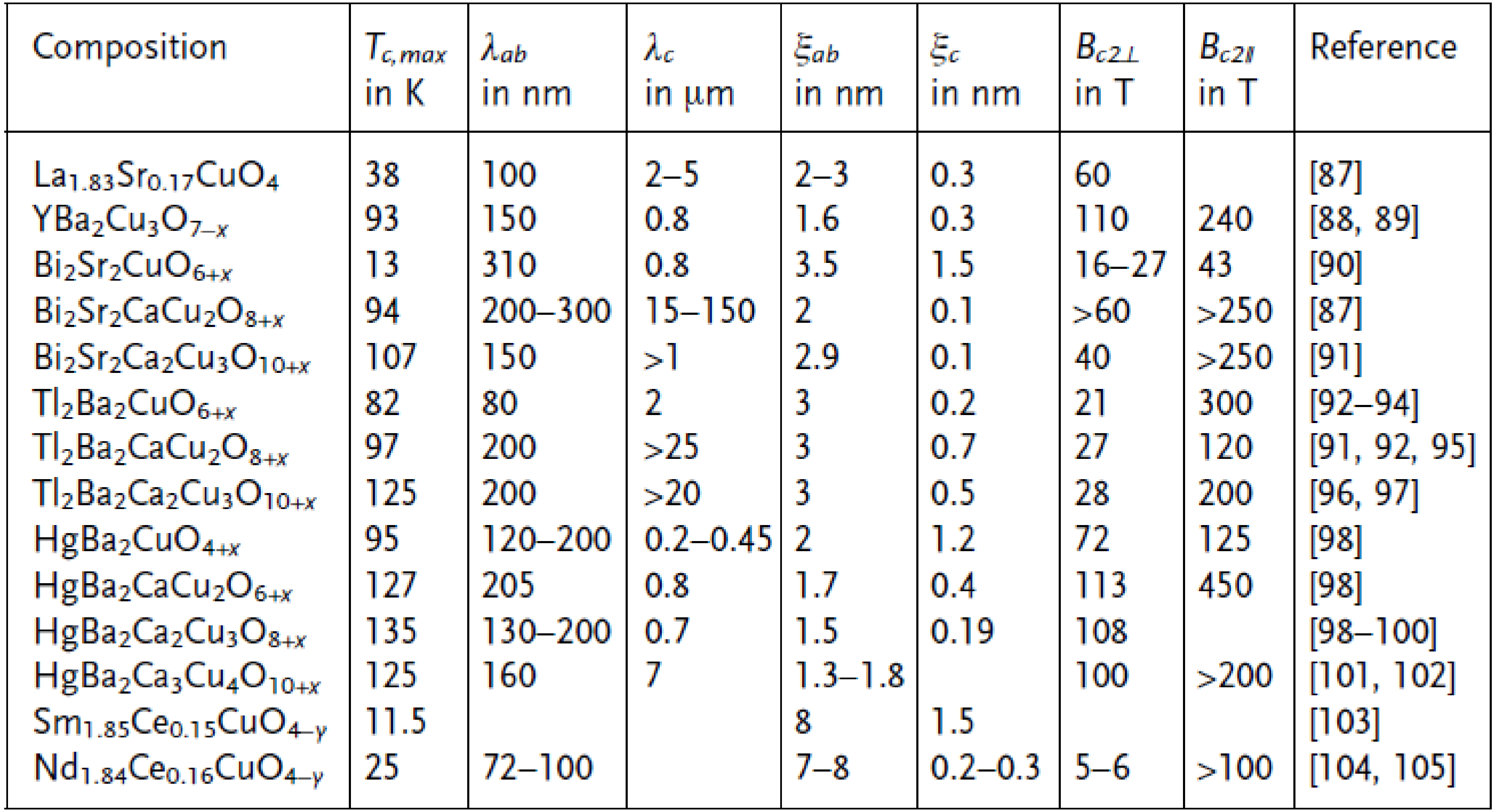


$YBa_2Cu_3O_7$



$Bi_2Sr_2CaCu_2O_8$

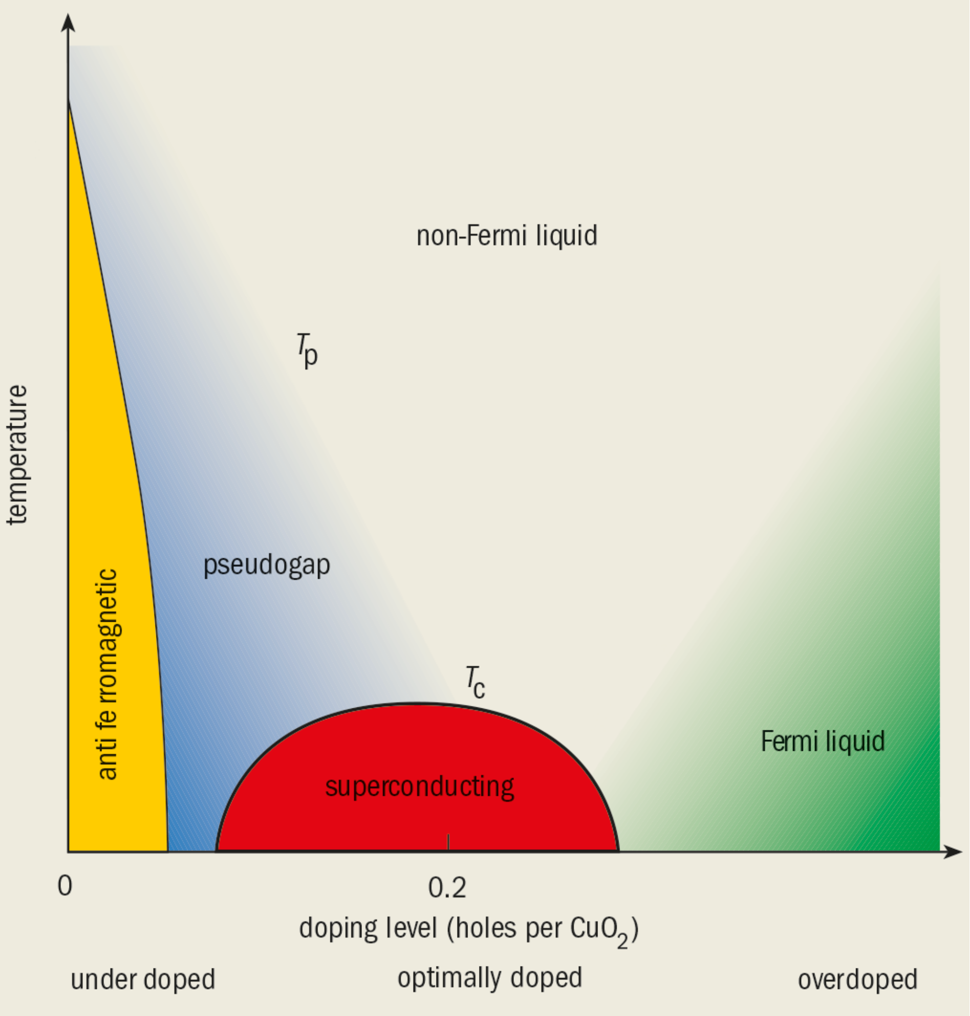
Characteristic data of Cuprate Superconductors



Composition	$T_{c,max}$ in K	λ_{ab} in nm	λ_c in µm	ξ_{ab} in nm	ξ_c in nm	$B_{c2\perp}$ in T	$B_{c2\parallel}$ in T	Reference
$La_{1.83}Sr_{0.17}CuO_4$	38	100	2–5	2–3	0.3	60		[87]
$YBa_2Cu_3O_{7-x}$	93	150	0.8	1.6	0.3	110	240	[88, 89]
$Bi_2Sr_2CuO_{6+x}$	13	310	0.8	3.5	1.5	16–27	43	[90]
$Bi_2Sr_2CaCu_2O_{8+x}$	94	200–300	15–150	2	0.1	>60	>250	[87]
$Bi_2Sr_2Ca_2Cu_3O_{10+x}$	107	150	>1	2.9	0.1	40	>250	[91]
$Tl_2Ba_2CuO_{6+x}$	82	80	2	3	0.2	21	300	[92–94]
$Tl_2Ba_2CaCu_2O_{8+x}$	97	200	>25	3	0.7	27	120	[91, 92, 95]
$Tl_2Ba_2Ca_2Cu_3O_{10+x}$	125	200	>20	3	0.5	28	200	[96, 97]
$HgBa_2CuO_{4+x}$	95	120–200	0.2–0.45	2	1.2	72	125	[98]
$HgBa_2CaCu_2O_{6+x}$	127	205	0.8	1.7	0.4	113	450	[98]
$HgBa_2Ca_2Cu_3O_{8+x}$	135	130–200	0.7	1.5	0.19	108		[98–100]
$HgBa_2Ca_3Cu_4O_{10+x}$	125	160	7	1.3–1.8		100	>200	[101, 102]
$Sm_{1.85}Ce_{0.15}CuO_{4-y}$	11.5			8	1.5			[103]
$Nd_{1.84}Ce_{0.16}CuO_{4-y}$	25	72–100		7–8	0.2–0.3	5–6	>100	[104, 105]

Characteristic data of different cuprate superconductors: maximum transition temperature, magnetic penetration depths λ_{ab} and λ_c for applied magnetic fields perpendicular and parallel to the layers, respectively, as well as the Ginzburg-Landau coherence lengths ξ_{ab} and ξ_c parallel and perpendicular to the CuO_2 layers, respectively. Also the upper critical fields for field orientations perpendicular and parallel to the planes, respectively, are given. In some cases, at low temperatures the upper critical fields are extremely high, and frequently they were extrapolated to low temperatures from the slope dB_{c2}/dT near the transition temperature.

Cuprates Phase Diagram



Cuprate phase diagram mystery The properties of the cuprates vary with temperature (y-axis) and the doping per unit cell of CuO_2 (x-axis). Theorists are unable to explain why the superconducting transition temperature (thick black line) is so high in the cuprates. However, if they could understand the behaviour of the cuprates in the pseudogap region (blue), they might be able to explain high-temperature superconductivity

*Bertram Batlogg and Chandra M Varma, **Physics World (2020), The underdoped phase** of cuprate **superconductors***

Cuprates VS Mathias rules

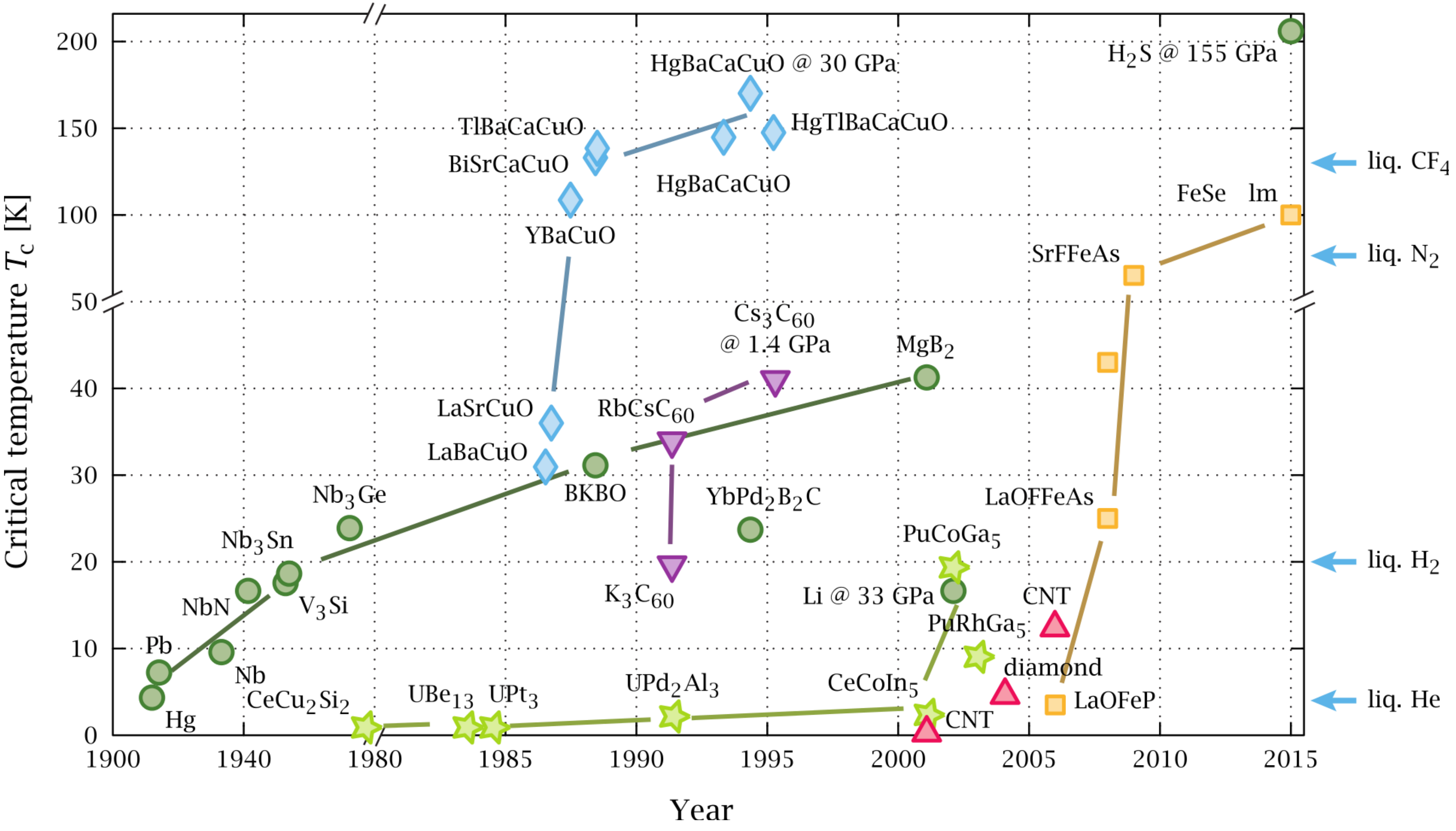
Mathias rules…

1. **High symmetry** is a good thing, cubic symmetry is best
2. **High density of electronic states** is a good thing
3. **Stay away** from **oxygen**
4. **Stay away** from **magnetism**
5. **Stay away** from **insulators**

Cuprates

1. Crystal structures do **not have high symmetry** and are **not cubic**
2. The **density of electronic states** is **not high**
3. **Oxygen content is high**
4. There is **proximity to a magnetic phase** in the phase diagram
5. "Relative" (non-gap-doped) **compounds are insulators**

Timeline of discovery of Superconductors



BCS

Heavy-fermions-based

Cuprate

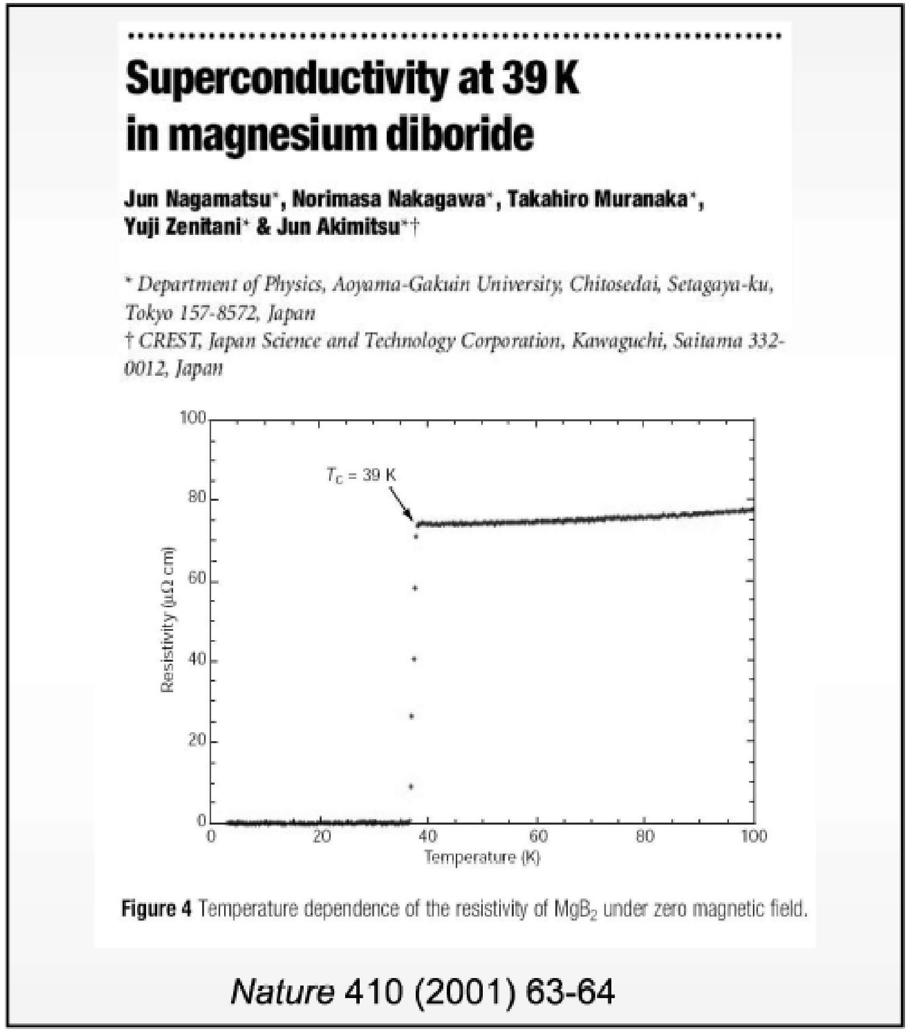
Buckminsterfullerene-based

Carbon-allotrope

Iron-pnictogen-based
(the new black)

Source: Wikipedia

Discovery of MgB_2 (2001)



Superconductivity at 39 K in magnesium diboride

Jun Nagamatsu*, Norimasa Nakagawa*, Takahiro Muranaka*, Yuji Zenitani* & Jun Akimitsu*†

** Department of Physics, Aoyama-Gakuin University, Chitosedai, Setagaya-ku, Tokyo 157-8572, Japan*
† CREST, Japan Science and Technology Corporation, Kawaguchi, Saitama 332-0012, Japan

Figure 4 Temperature dependence of the resistivity of MgB_2 under zero magnetic field.

Nature 410 (2001) 63-64

No sleep: Akimitsu opens the session at Seattle.

Genie in a bottle

Robert J. Cava

An overlooked compound has a surprise in store for physicists. It becomes superconducting at a much higher temperature than any other stable metallic compound.

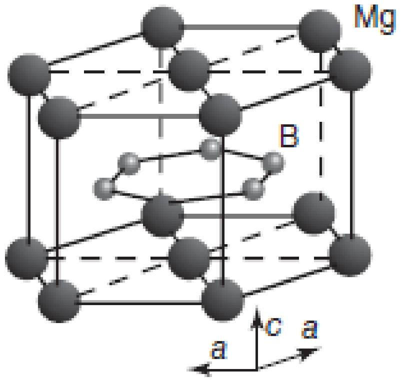
The field of superconductivity has been rocked by a startling announcement. For fifteen years, researchers have been delving into the mysterious and complex world of high-temperature superconducting materials — virtually ignoring simple metallic compounds because they superconduct at very low temperatures. But now Akimitsu and colleagues have discovered superconductivity at an amazing 39 degrees above absolute zero in the simple compound magnesium boride (MgB_2). They report their discovery on page 63 of this issue[1], in what must be one of the shortest communications published in *Nature* in recent memory.

Superconductors are materials that lose their resistance to electrical current flow below a certain critical temperature (T_c). In the ideal case, this zero-resistance state is

Figure 1 The newly discovered superconductor magnesium boride has been available in large quantities from suppliers of inorganic chemicals for many years, but physicists have finally 'rubbed the lamp' and found that magnesium boride superconducts at an amazing 39 K (ref. 1).

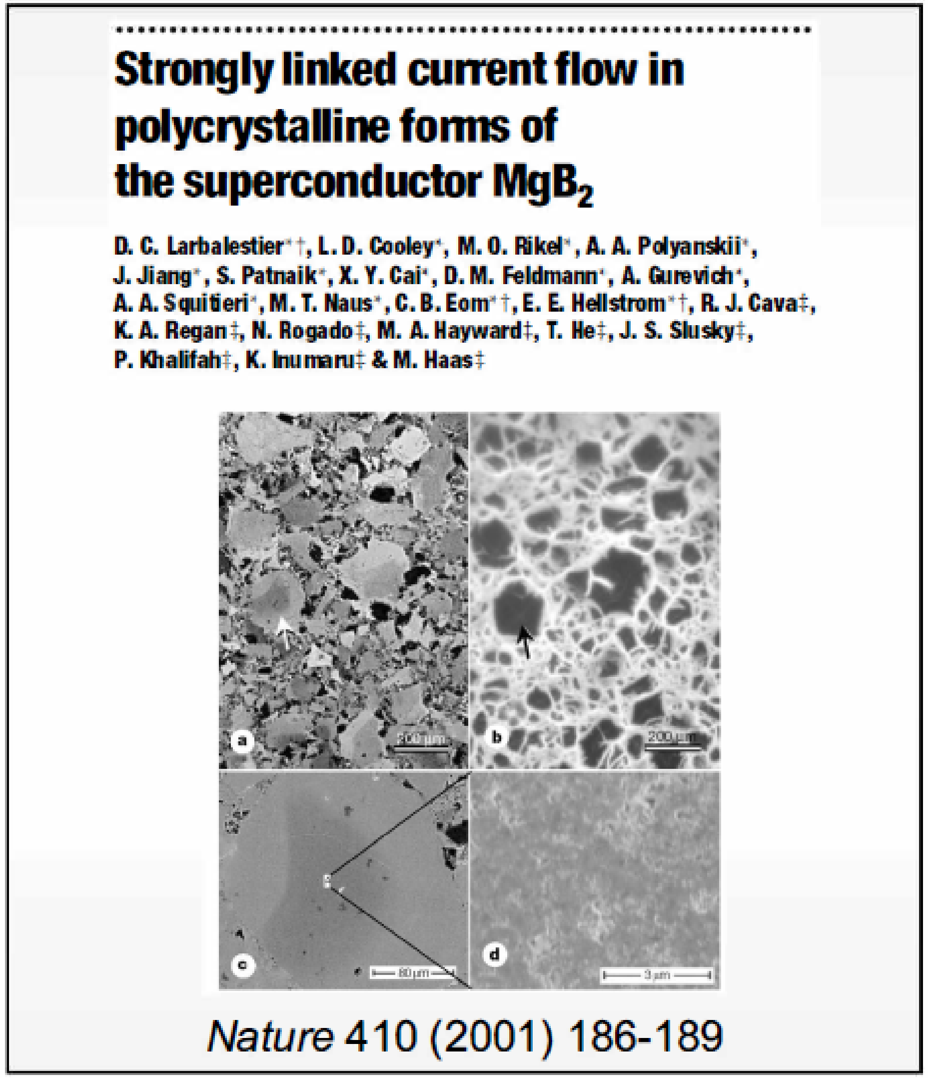
Nature 410 (2001) 23-24

Discovery of MgB_2 (2001)



Double gap

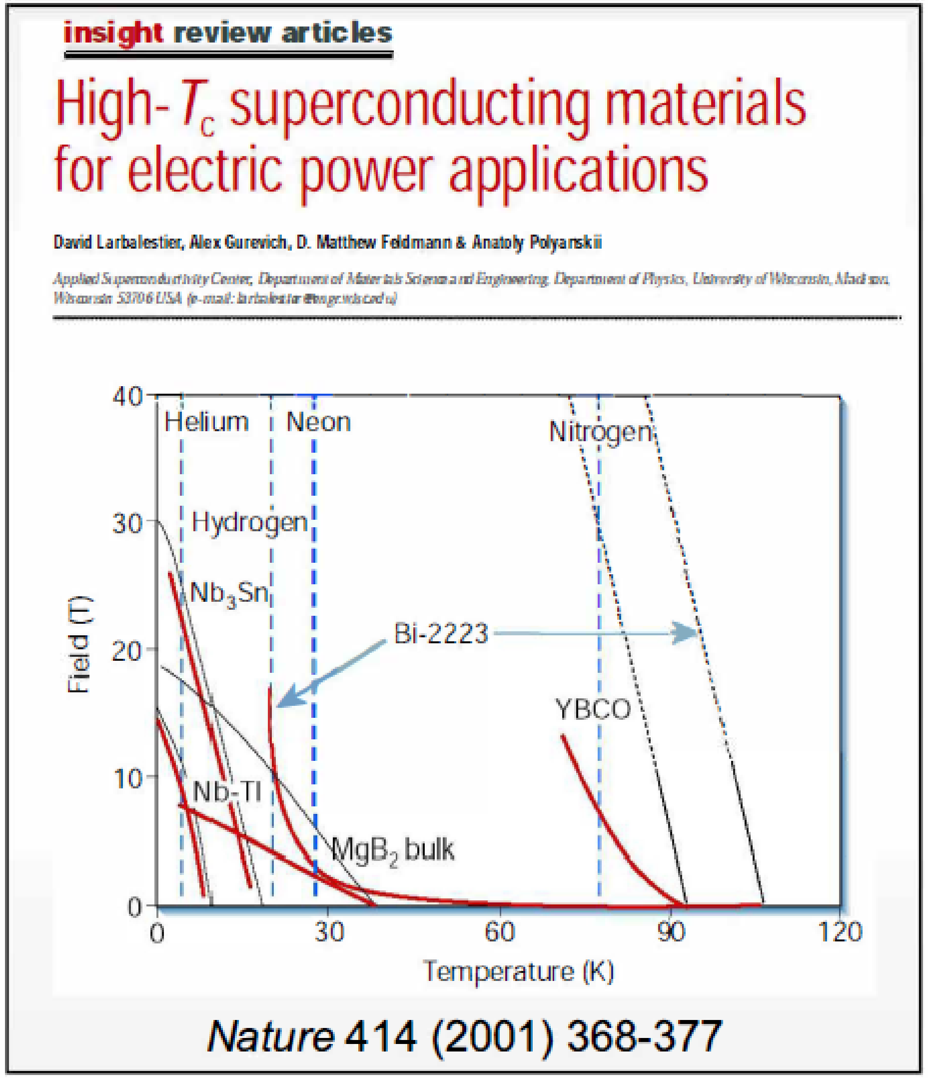
Superconductor



Strongly linked current flow in polycrystalline forms of the superconductor MgB_2

D. C. Larbalestier*†, L. D. Cooley*, M. O. Rikel*, A. A. Polyanskii*, J. Jiang*, S. Patnaik*, X. Y. Cai*, D. M. Feldmann*, A. Gurevich*, A. A. Squitieri*, M. T. Naus*, C. B. Eom*†, E. E. Hellstrom*†, R. J. Cava‡, K. A. Regan‡, N. Rogado‡, M. A. Hayward‡, T. He‡, J. S. Slusky‡, P. Khalifah‡, K. Inumaru‡ & M. Haas‡

Nature 410 (2001) 186-189



insight review articles

High-T_c superconducting materials for electric power applications

David Larbalestier, Alex Gurevich, D. Matthew Feldmann & Anatoly Polyanskii

Applied Superconductivity Center, Department of Materials Science and Engineering, Department of Physics, University of Wisconsin, Madison, Wisconsin 53706 USA (e-mail: larbalestier@engr.wisc.edu)

Nature 414 (2001) 368-377

Superconductors at room Temperature

LK-99 (*born* July 2023, *died* August 2023)

In July 2023, a group of South Korean researchers with two Arxiv publications announced that they had produced a superconductor with Tc of 400k at atmospheric pressure!

- https://arxiv.org/ftp/arxiv/papers/2307/2307.12037.pdf
- https://arxiv.org/ftp/arxiv/papers/2307/2307.12008.pdf

Sending the article to David Larbastier, a colleague commented as follows:
«Where would you place these authors on a scale from "shameless frauds" to "overenthusiastic scientists"? »

In less than a month, dozens of Research Centers replicated the results and proved that it was a fake! The material is an insulator and the magnetic levitation was a result of its ferroelectric properties due to the presence of copper sulfide impurities

https://www.nature.com/articles/d41586-023-02585-7

Superconductors at room Temperature

Andrea Cavalleri, Max Plank Institute, Hamburg (2014)

YBCO irradiated with IR pulses @SLAC

The oscillation of the lattice can be modulated

A **metastable state** is obtained for few picoseconds

W. Hu, S. Kaiser, D. Nicoletti, C. R. Hunt, I. Gierz, M. C. Hoffmann, M. Le Tacon, T. Loew, B. Keimer & A. Cavalleri
Optically enhanced coherent transport in $YBa_2Cu_3O_{6.5}$ by ultrafast redistribution of interlayer coupling
Nature Materials, published online: 11 May 2014 | doi:10.1038/nmat3963

Bibliography of this part

- W. Buckel, R. Kleiner, "*Superconductivity - Fundamentals and Applications*", Wiley
  Chapter 2 - Superconducting Elements, Alloys, and Compounds

- K. Fossheim, A. Sudbø, "*Superconductivity - Physics and applications*", Wiley
  Chapter 2 - Superconducting materials