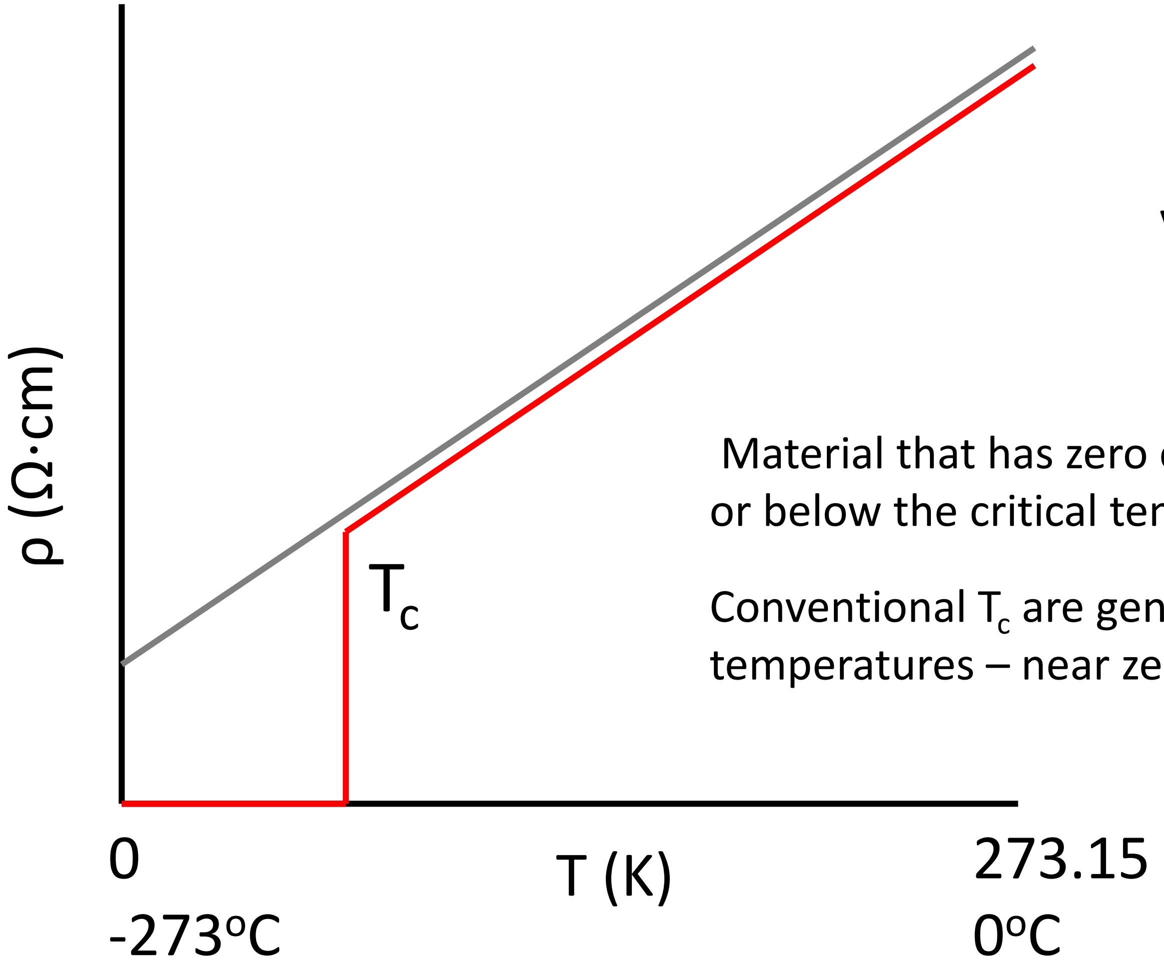
Superconductivity

Outline

- Superconductivity
  - conventional superconductors
  - properties
  - theory
- Cuprate Superconductors
  - YBCO
  - structures
  - synthesis

Superconductivity



$R=0$

$P=I^2R$

$V=IR$, $V=0$

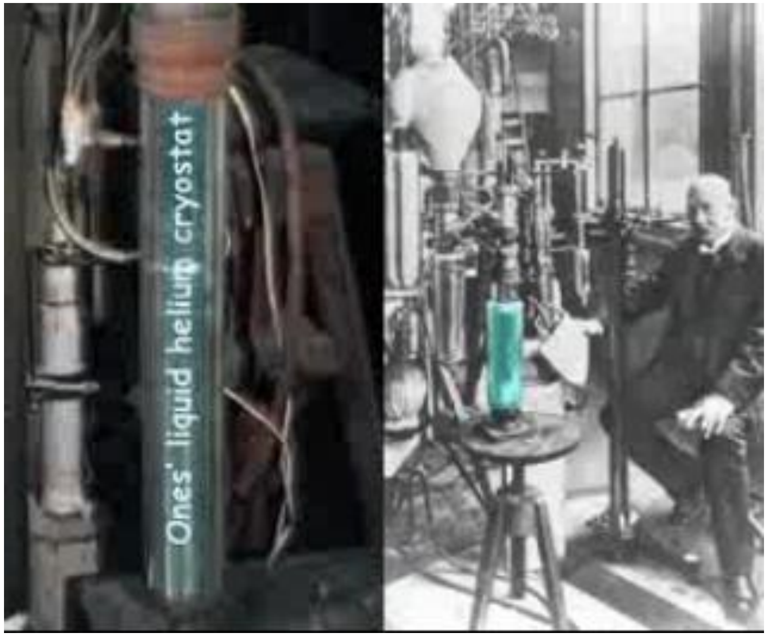
Material that has zero electrical resistance at or below the critical temperature, T_c

Conventional T_c are generally low temperatures – near zero K

Superconductors - History

- Heike Kammerlingh Onnes liquifies He in 1908 (boiling point = 4.19 K)
- Discovers resistance of Hg drops abruptly to zero at 4.19 K (April 8, 1911)
- Won Nobel Prize in 1913
- Opens doors for low

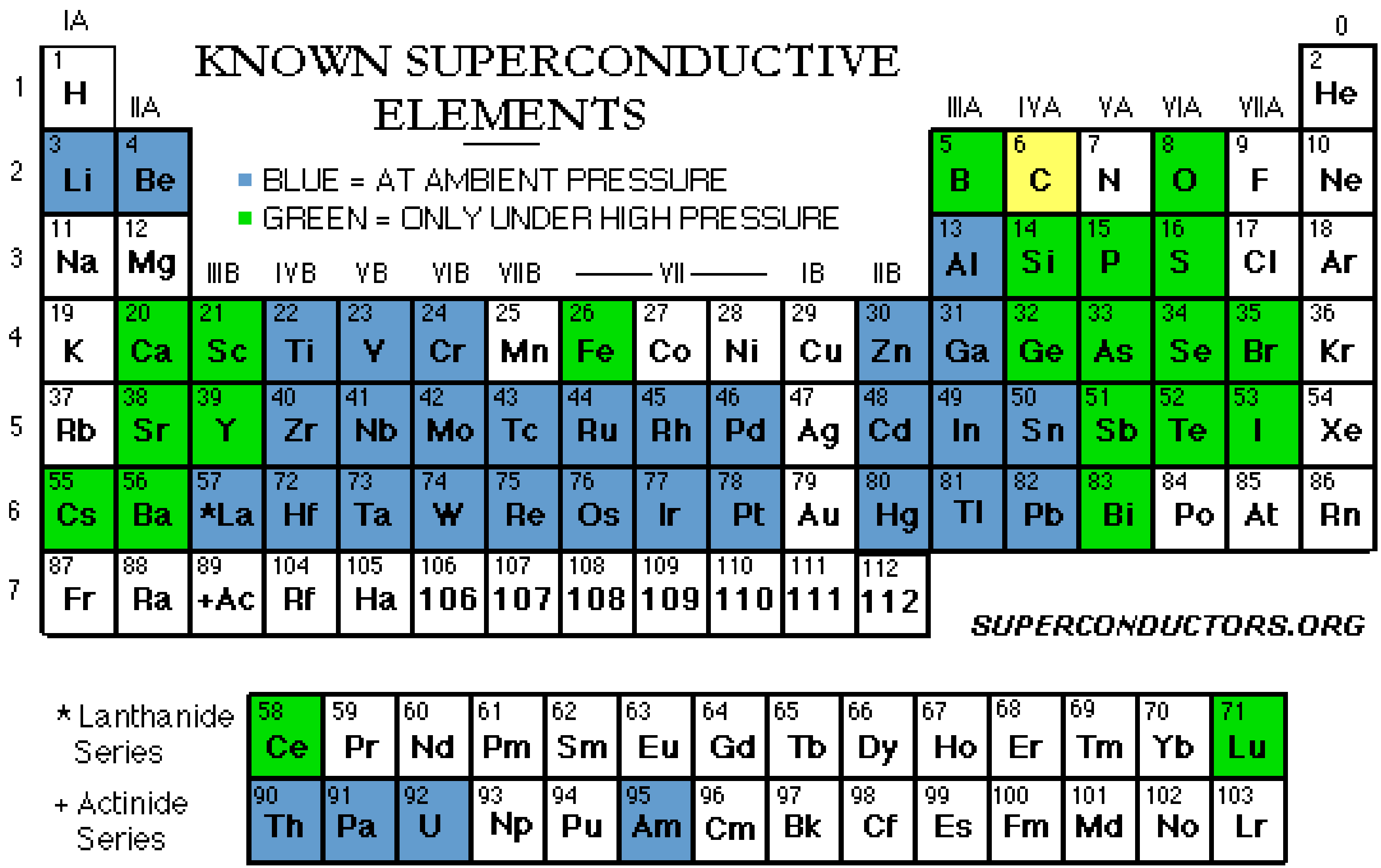
temperature research



http://www.msm.cam.ac.uk/ascg/lectures/materials2/leadbismuth.php

http://www.msm.cam.ac.uk/ascg/lectures/fundamentals/isotope.php?video=flash

Elemental Superconductors



http://superconductors.org/Type1.htm

Elemental Superconductors

Lead (Pb)	**7.196 K**	**Zirconium (Zr)**	**0.61 K**
Lanthanum (La)	**4.88 K**	**Americium (Am)**	**0.60 K**
Tantalum (Ta)	**4.47 K**	**Cadmium (Cd)**	**0.517 K**
Mercury (Hg)	**4.15 K**	**Ruthenium (Ru)**	**0.49 K**
Tin (Sn)	**3.72 K**	**Titanium (Ti)**	**0.40 K**
Indium (In)	**3.41 K**	**Uranium (U)**	**0.20 K**
Thallium (Tl)	**2.38 K**	**Hafnium (Hf)**	**0.128 K**
Rhenium (Re)	**1.697 K**	**Iridium (Ir)**	**0.1125 K**
Protactinium (Pa)	**1.40 K**	**Tungsten (W)**	**0.0154 K**
Aluminum (Al)	**1.175 K**	**Lithium (Li)**	**0.0004 K**
Molybdenum (Mo)	**0.915 K**	**Rhodium (Rh)**	**0.000325 K**

http://superconductors.org/Type1.htm

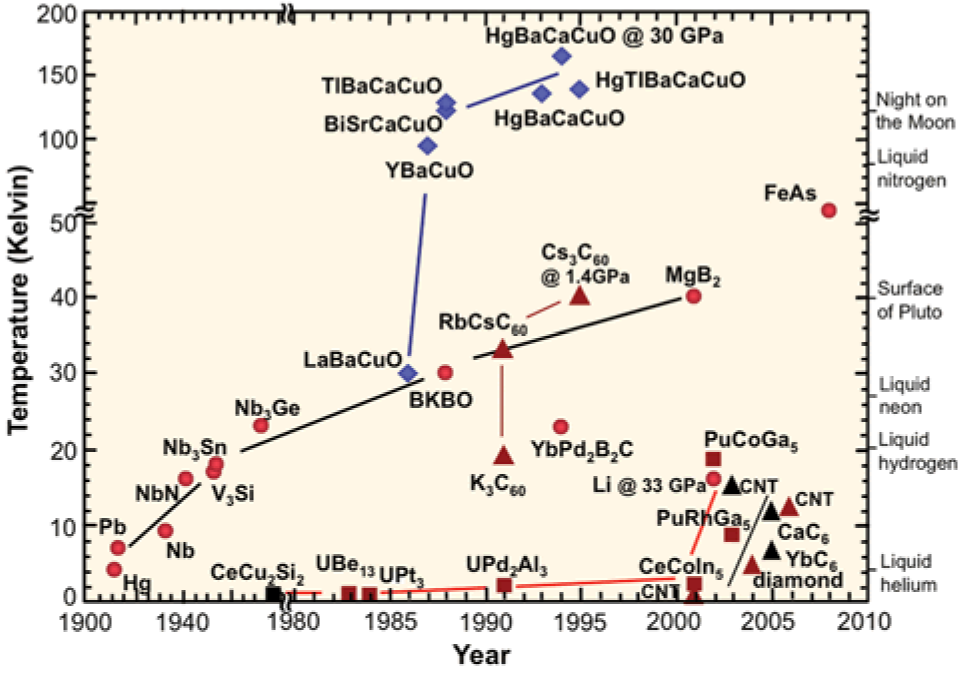
Compound Superconductors

Nb_3Ge	23.2 K	V_3Si	17.1 K
Nb_3Ga	20.3 K	V_3Ga	16.5 K
Nb_3Al	18.6 K	NbN	17.3 K
Nb_3Sn	18.0 K	MoC	14.3 K
Nb_3Au	10.8 K	$NbSe_2$	7.2 K

Nb_3Ge held record for highest T_c superconductor until 1986

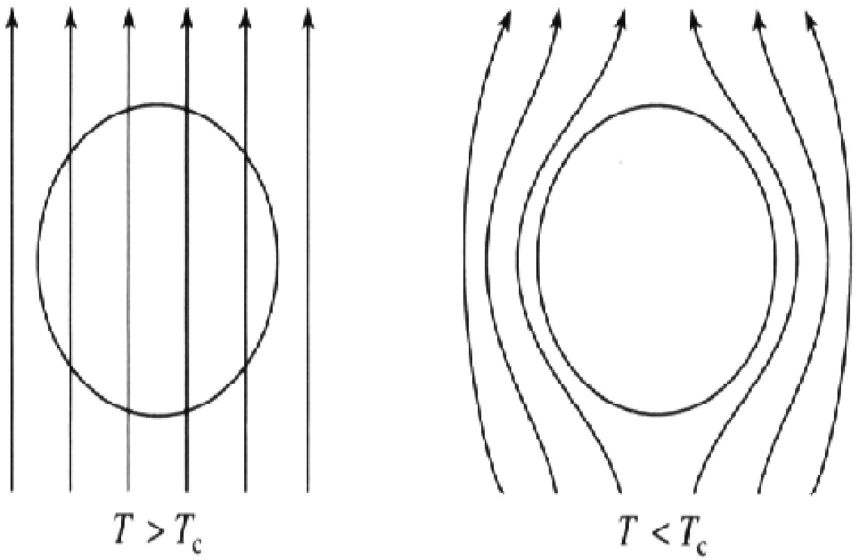
Burns, Gerald. High-Temperature Superconductivity: An Introduction

Historical Development of Superconductor

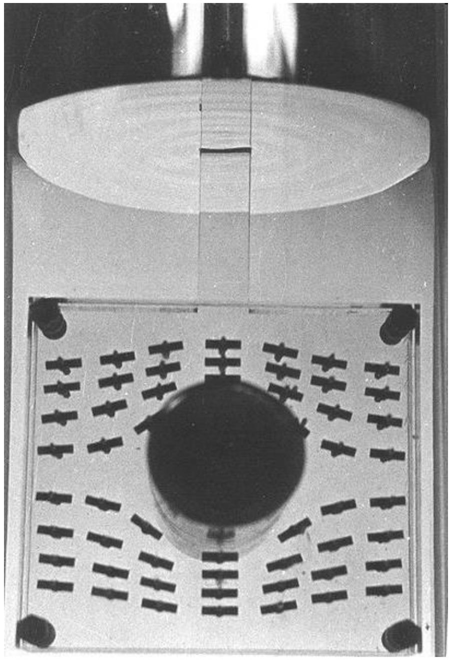


Superconducting Properties

- Zero resistance – gives rise to Meissner Effect (1933)
- In weak magnetic field, magnetic field bends around material



http://www.thesuperconductor.info/images/untitled.bmp

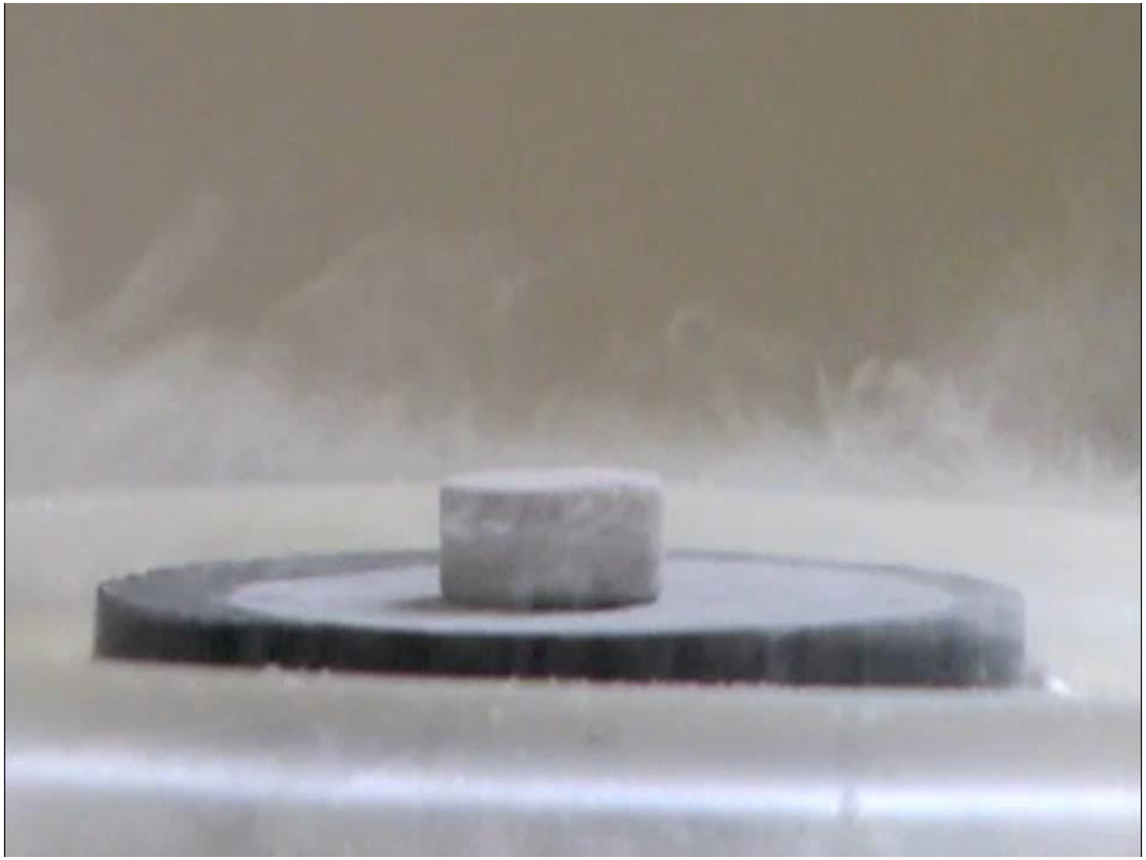


http://en.wikipedia.org/wiki/Meissner_effect

- If magnetic field > critical magnetic field (H_c), magnetic field penetrates and superconductivity is lost

Meissner effect

a metal is cooled and become superconducting. A magnet on top of it is *lifted* because the superconductor expels magnetic fields. This is the Meissner effect.



http://sdphln.ucsd.edu/~jorge/meissner/meissnerexp.html

Applications - Transportation

- Trains “float” on superconducting magnets, almost eliminating friction

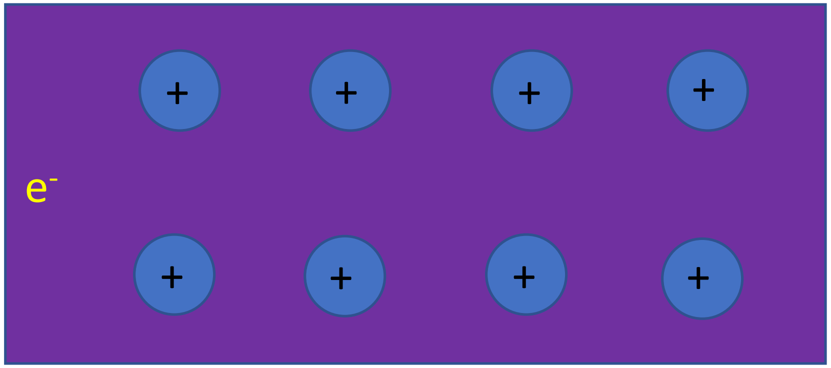
Yamashi Maglev Test Line - Reached 361 mph Dec 2003

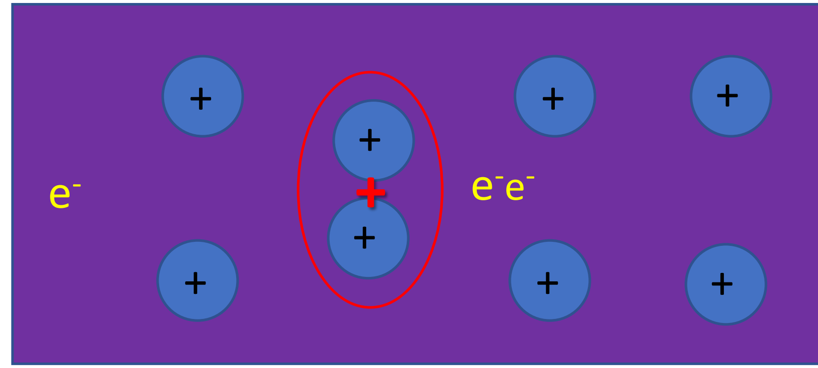
http://superconductors.org/Uses.htm

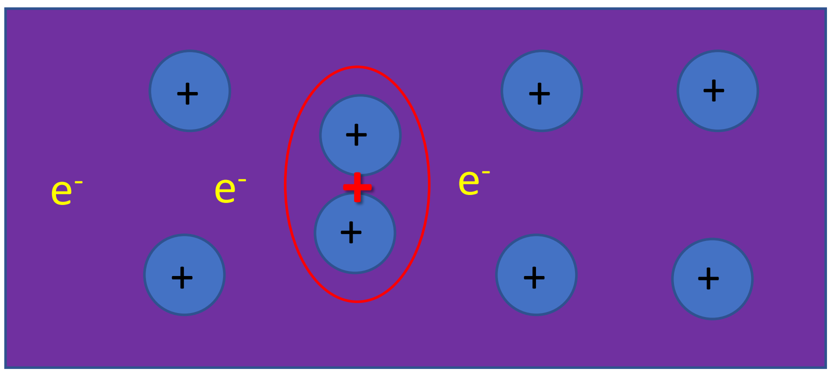
BCS Theory

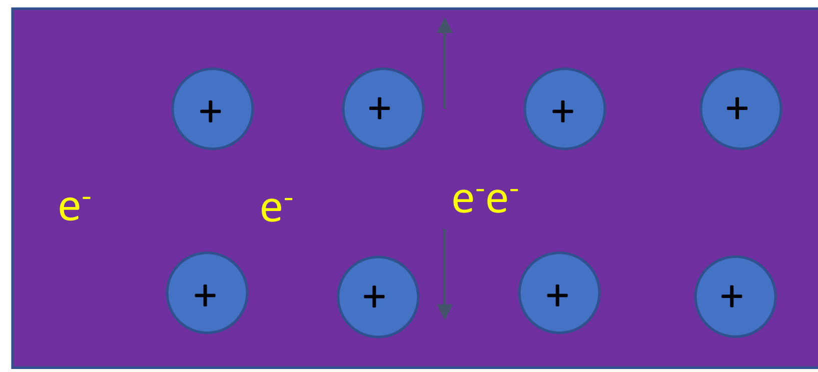
- Bardeen-Cooper-Schrieffer – BCS Theory: 1957
- Nobel Prize in 1972
- Correctly predicts superconducting properties
- Proposes that e^- move as Cooper pairs from e^- -phonon interaction
  - e^- moves through crystal by distorting structure (via phonon)
  - 2nd e^- lowers its energy by moving with it through distorted structure
  - http://superconductors.org/bcs_anim.gif

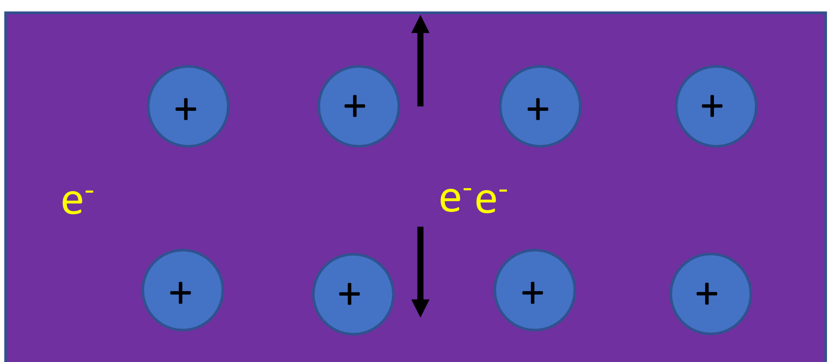
BCS Theory





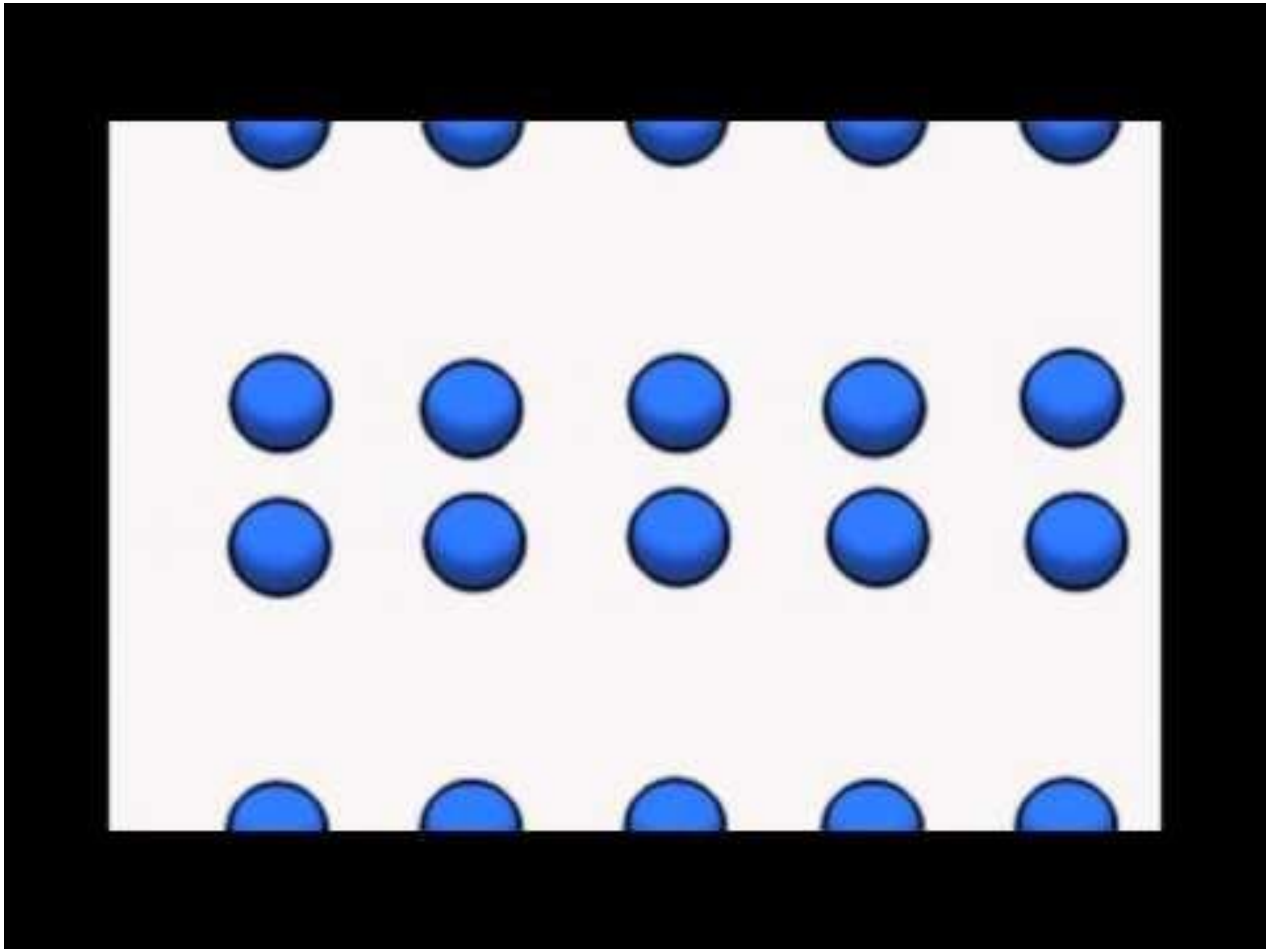






- BCS theory predict an upper limit on T_c is 30K which is in agreement with Nb_3Ge (23.3 K)

Phonons



Phonons are responsible for the propagation of sound in a solid (Speed of sound)

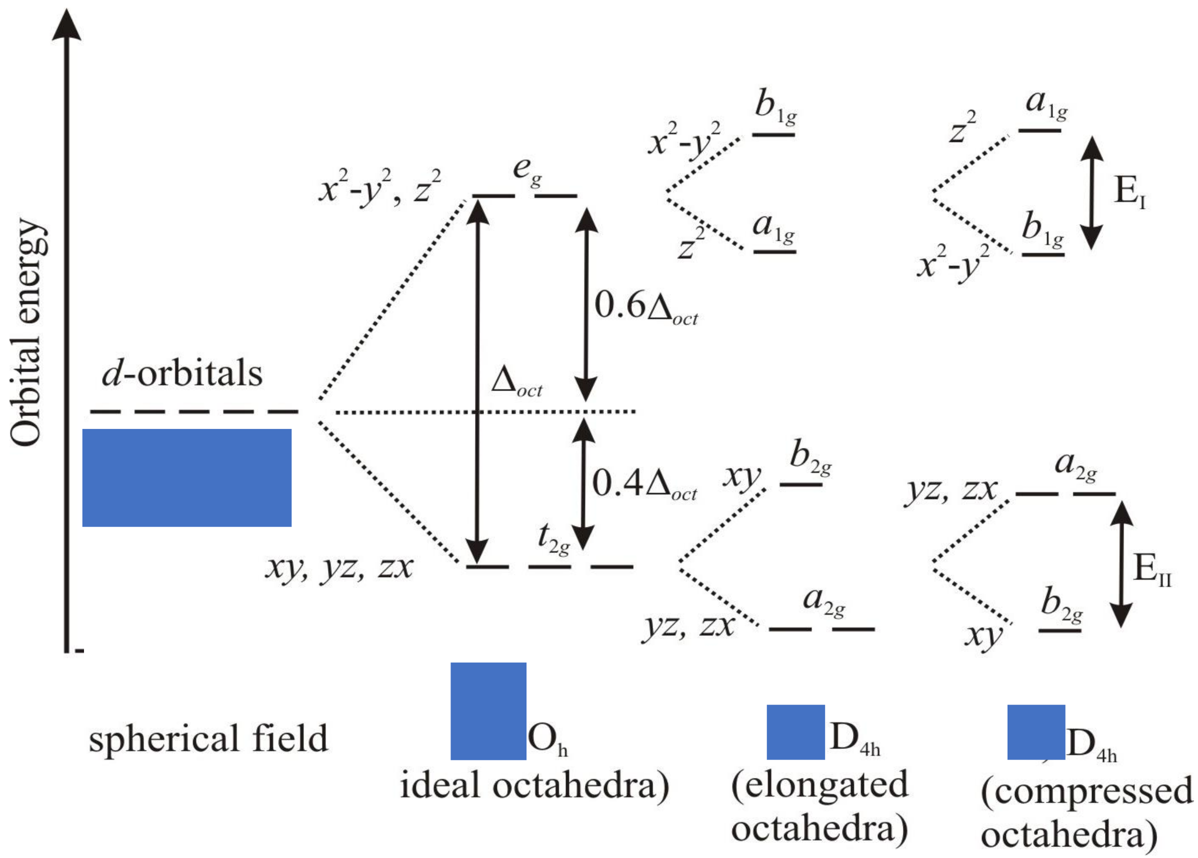
Phonons are responsible for the transfer of heat in the solid (Thermal conductivity)

First Cuprate Superconductor

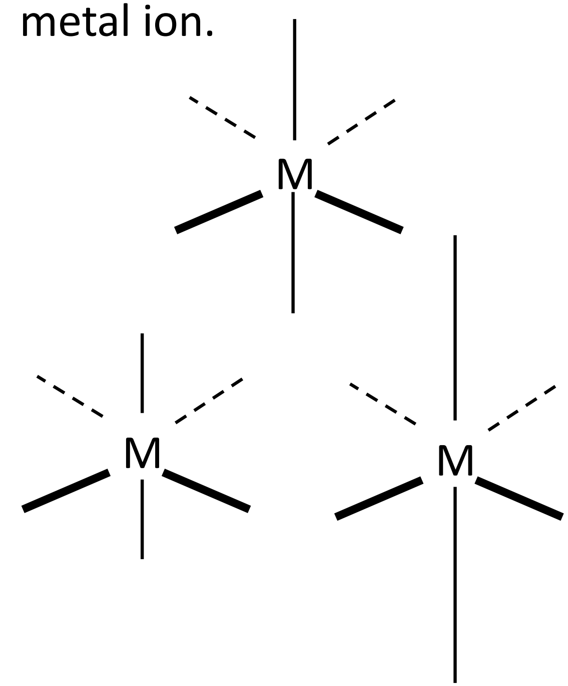
- Compound that exhibits with CuO_4 anion
- Discovered by Bednorz & Müller at IBM Research Lab in Zurich, Switzerland in 1986
- La_2CuO_4 doped with Ba^{2+} → $T_c > 30$ K
- Believed higher T_c were possible by enhancing e^- - phonon interactions through Jahn-Teller effects
- Opened door again for superconductivity – won Nobel Prize in 1987

Bednorz, J.G. and Müller, K.A. *Z. Phys. B* **1986**, *64*, 189-193

Jahn-Teller Distortion



6 ligands are arranged in an octahedral fashion around the metal ion.



In octahedral symmetry the *d*-orbitals split into two sets with an energy difference Δ_{oct} where the dxy, dxz and dyz orbitals will be lower in energy than the dz^2 and dx^2-y^2

Further splitting of the energy levels can result from the transition from O_h to tetragonal symmetry (D_{4h}), e.g. by elongation or compression of the octahedron along along *z*-direction.

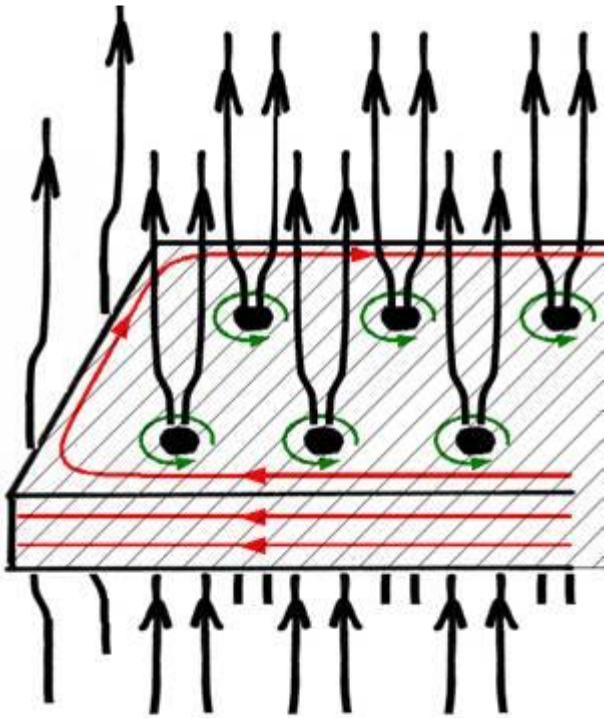
Jahn-Teller Distortion in Cuprates

- Cu = [Ar]$3d^{10}4s^{1}$, 4s e- is most weakly bound in the solid state
- Generally Cu^{2+}, [Ar]$3d^{9}$ configuration, subject to 1st order Jahn-Teller distortions
- M - O_p bond < M - O_z bond
- M - $O_p \approx$ 1.89 - 1.94 Å
- M - $O_z \approx$ 2.41 Å
- Shows Jahn-Teller distortions - increase e^--phonon coupling parameter, increase T_c

Type I vs Type II Superconductors

Type I	Type II
Elements or alloys	Contain metal-oxide (mostly cuprates)
Low T_c values (< 30 K)	High T_c values (> 30 K)
Meissner State	Mixed Meissner State
One $H_{c:}$ $H < H_c$ = magnetic field does not penetrate $H > H_c$ = magnetic field completely penetrates	Two H_c: $H < H_{c1}$ = magnetic field does not penetrate $H_{c1}<H<H_{c2}$ = a range of magnetic field partially penetrates $H > H_{c2}$ = magnetic field completely penetrates

Mixed Meissner State



Black arrows = applied external magnetic field

Red arrows = superconducting currents produced in superconductor to screen against black arrows

Green arrows = other superconducting currents that create vortices that allow part of the applied magnetic field through

Vortices are pinned (flux pinning), which keep a levitating magnet in place and allows rotation on only one axis

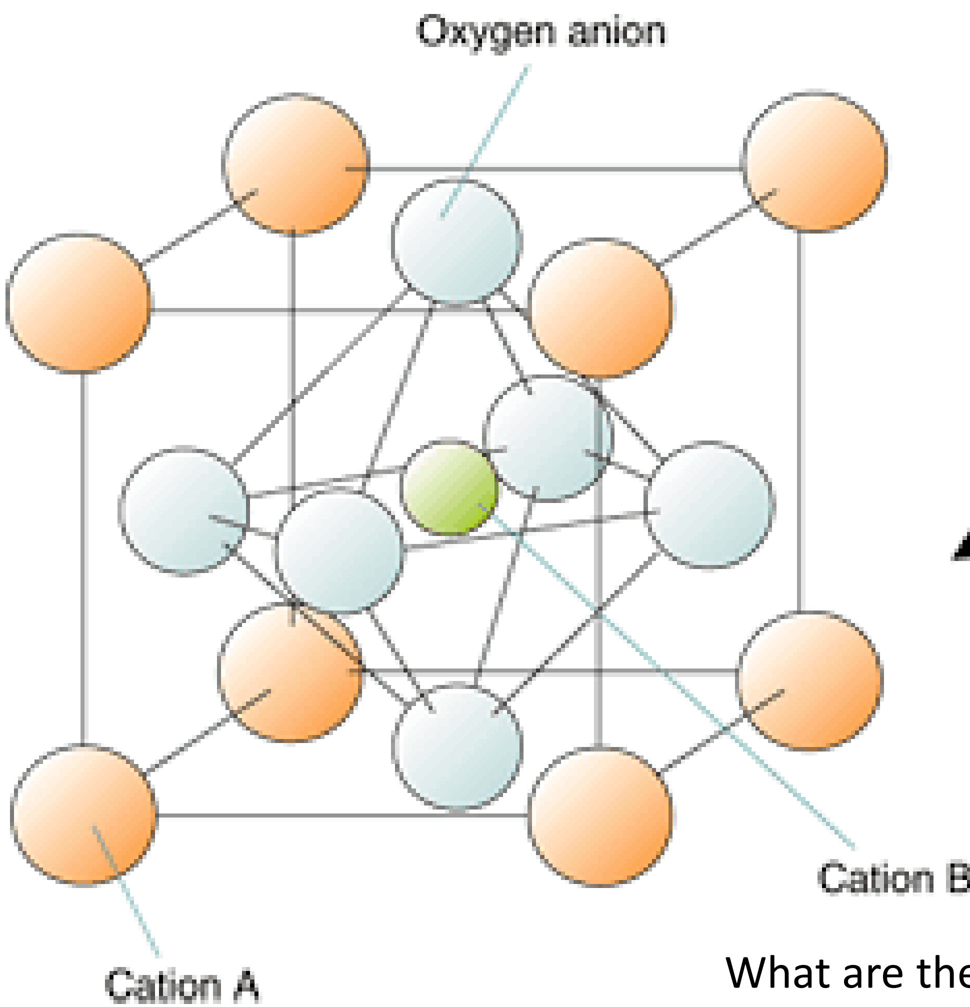
http://www.supraconductivite.fr/en/index.php?p=supra-levitation-vortex-more

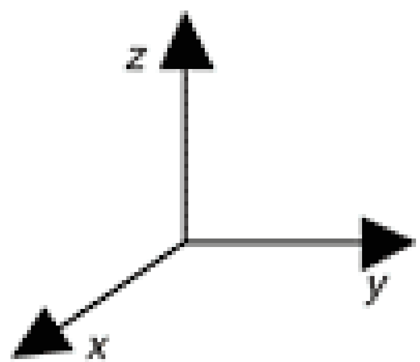
Cuprate Structure

- Adopt perovskite-like structure
- Perovskite = $CaTiO_3$
- Cu replaces Ti^{4+} (B cation)
  - Cu^{2+} (VI) = .73 Å Ti^{4+} (VI) = .605 Å
- Multiple possible replacements for Ca:
  - Y, Tl, Bi, Sr, Ba, La

Shannon, R; *Acta Crystallogr*, *Sect A.* **1976**, *32*, 751

Perovskite Structure





How many A cations are present?

How many B cations are present?

How many O anions are present?

What are the coordination numbers for each atom?

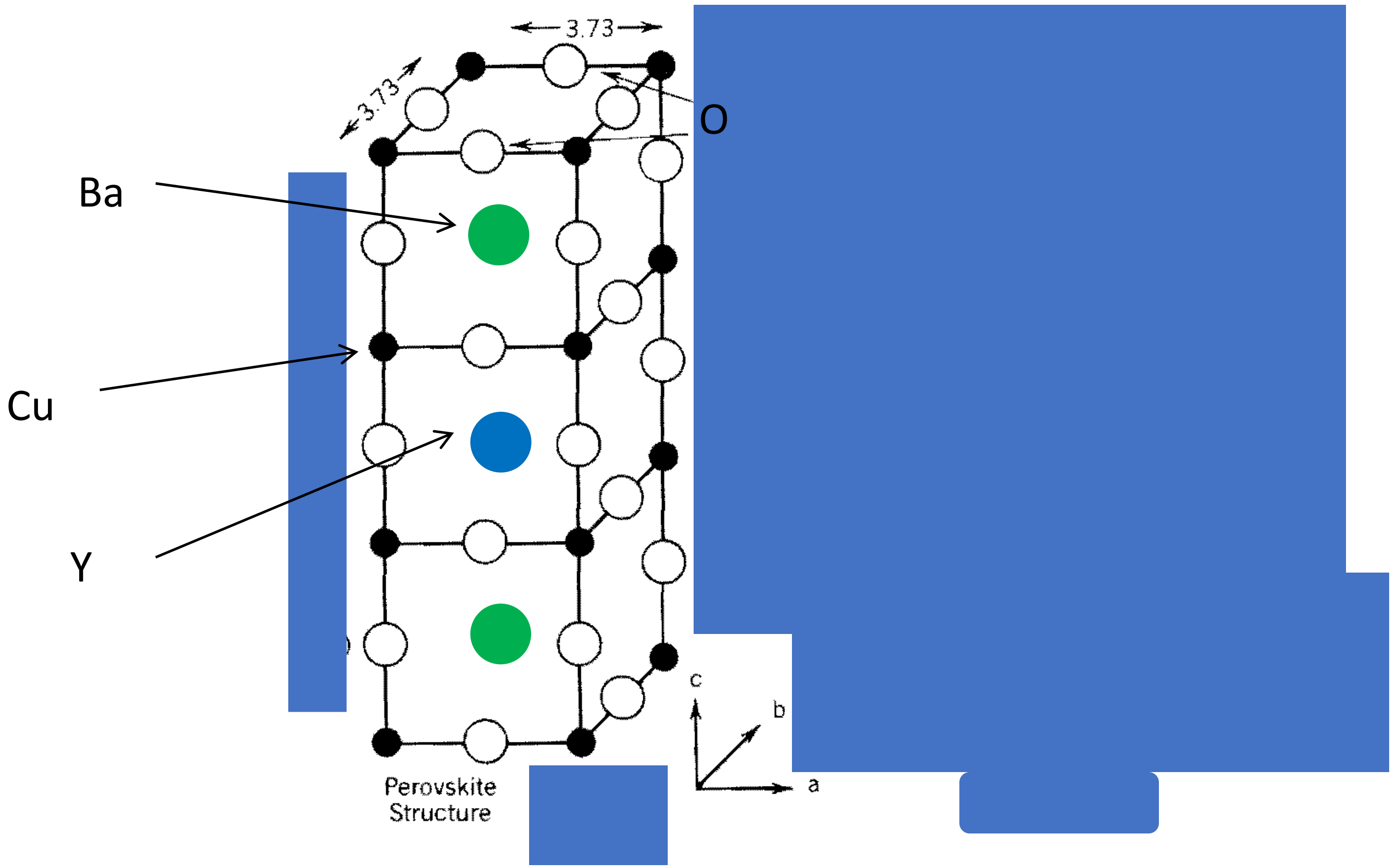
https://www.ntt-review.jp/archive_html/200709/images/sp1_fig01.gif

$YBa_2Cu_3O_7$ (YBCO)

- YBCO perovskite based super conductor
- YBCO was first superconductor with T_c > 77 K (T_c of up to 93 K)
- Discovered by Maw-Kuen Wu at University of Alabama
- What is the oxidation state of Cu?
  - Mixture of 2Cu(II) and 1Cu(III)

Wu, M. *et al. Phys. Rev. Lett.* **1987**, *58*, 908.

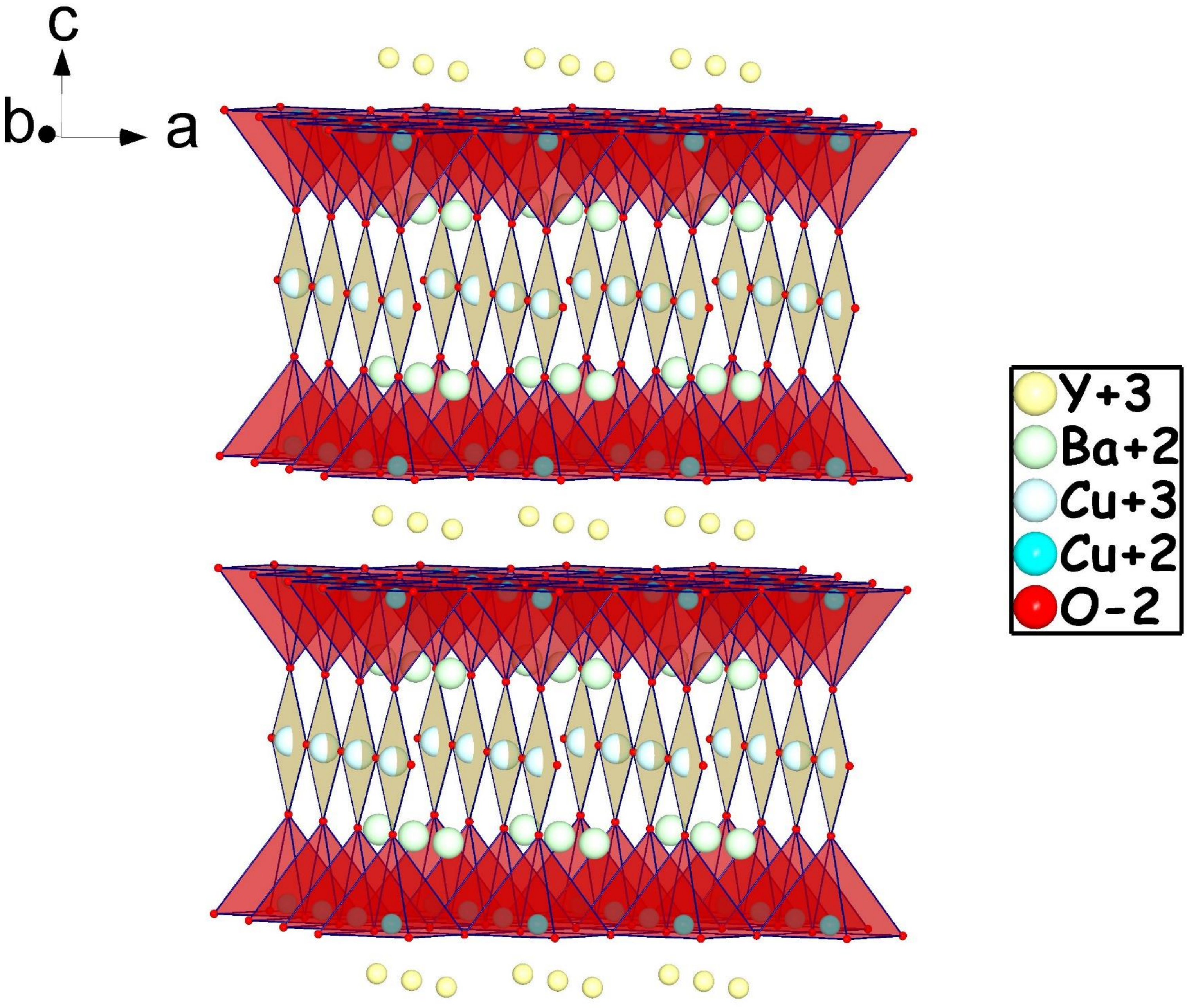
YBCO Structure



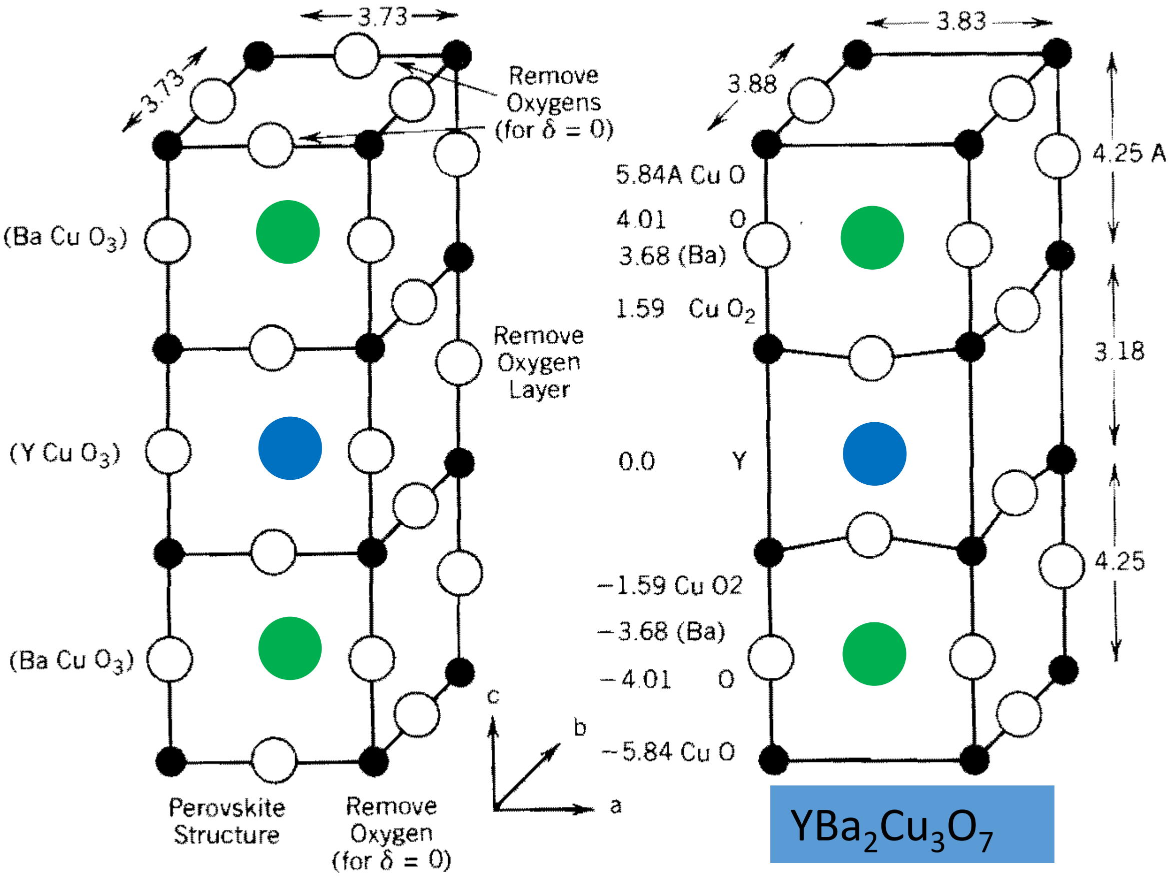
How many Y, Ba, Cu, and O atoms are in the unit cell?

$YBa_2Cu_3O_9$ 3 x ABO_3, where A = Y or Ba, B = Cu

Poole, Charlse. Copper Oxide Superconductors


c
b
a
Y+3
Ba+2
Cu+3
Cu+2
O-2

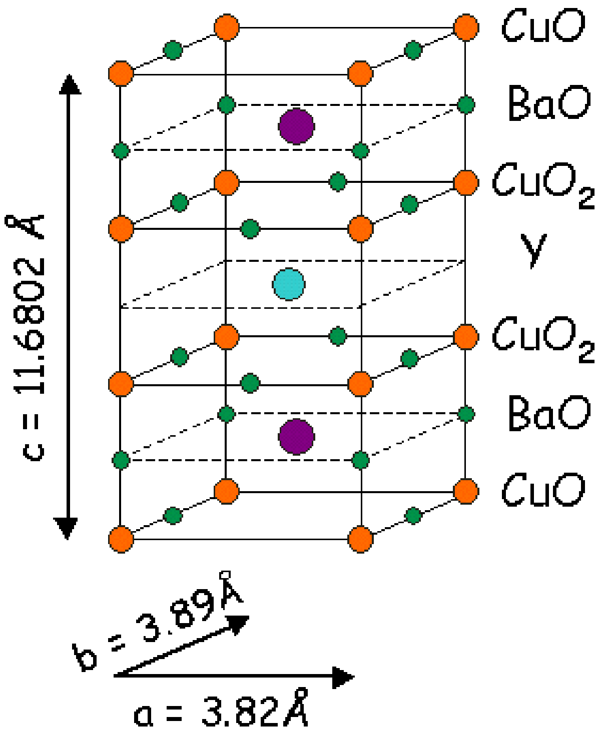
YBCO Structure

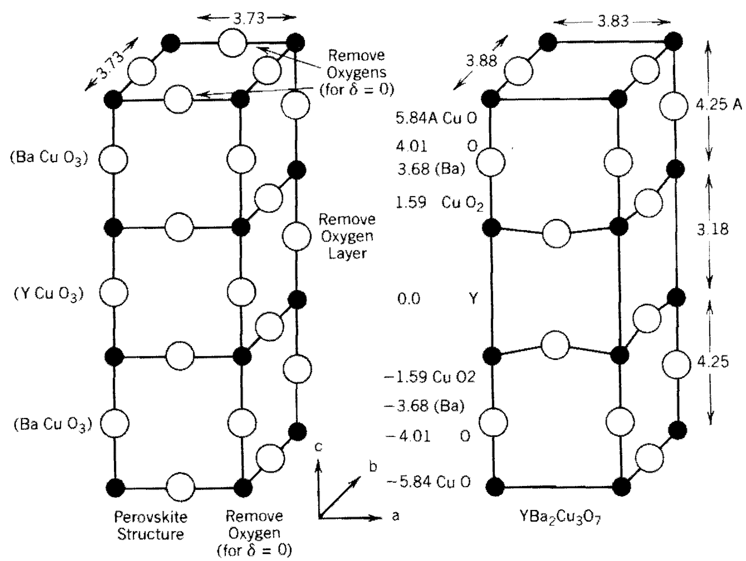


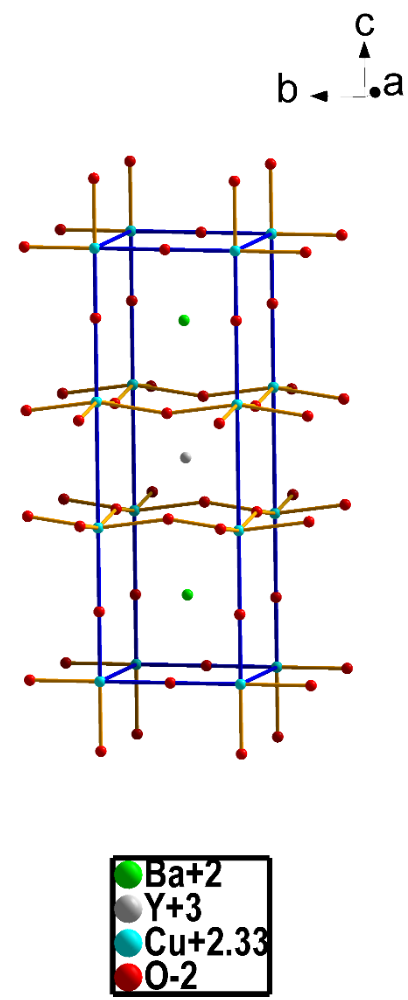
How many oxygen atoms are in the stoichiometric oxygen deficient perovskite unit cell?

Poole, Charlse. Copper Oxide Superconductors

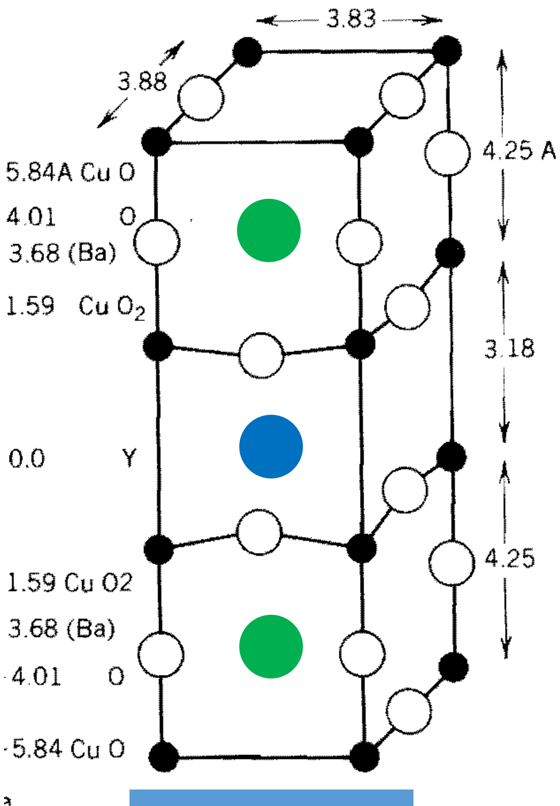
The structure of YBCO





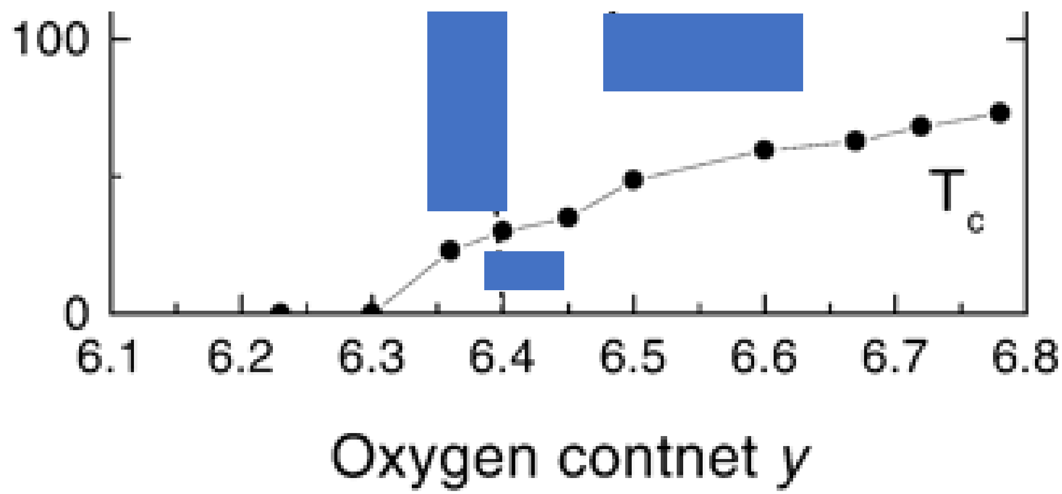


T_C vs. Oxygen Content



$YBa_2Cu_3O_7$

$\delta=0$



$YBa_2Cu_3O_{7-\delta}$

Nomenclature

1201, 1212, 1223

- Last digit = # of CuO_2 layers (n)
- First two digits = ratio of two metals occupying the A-site
- Digit before n = # of cations that separate adjacent CuO_2 layers (= n – 1)

1201	$TlBa_2CuO_5$
1212	$TlBa_2CaCu_2O_7$
1223	$TlBa_2Ca_2Cu_3O_9$

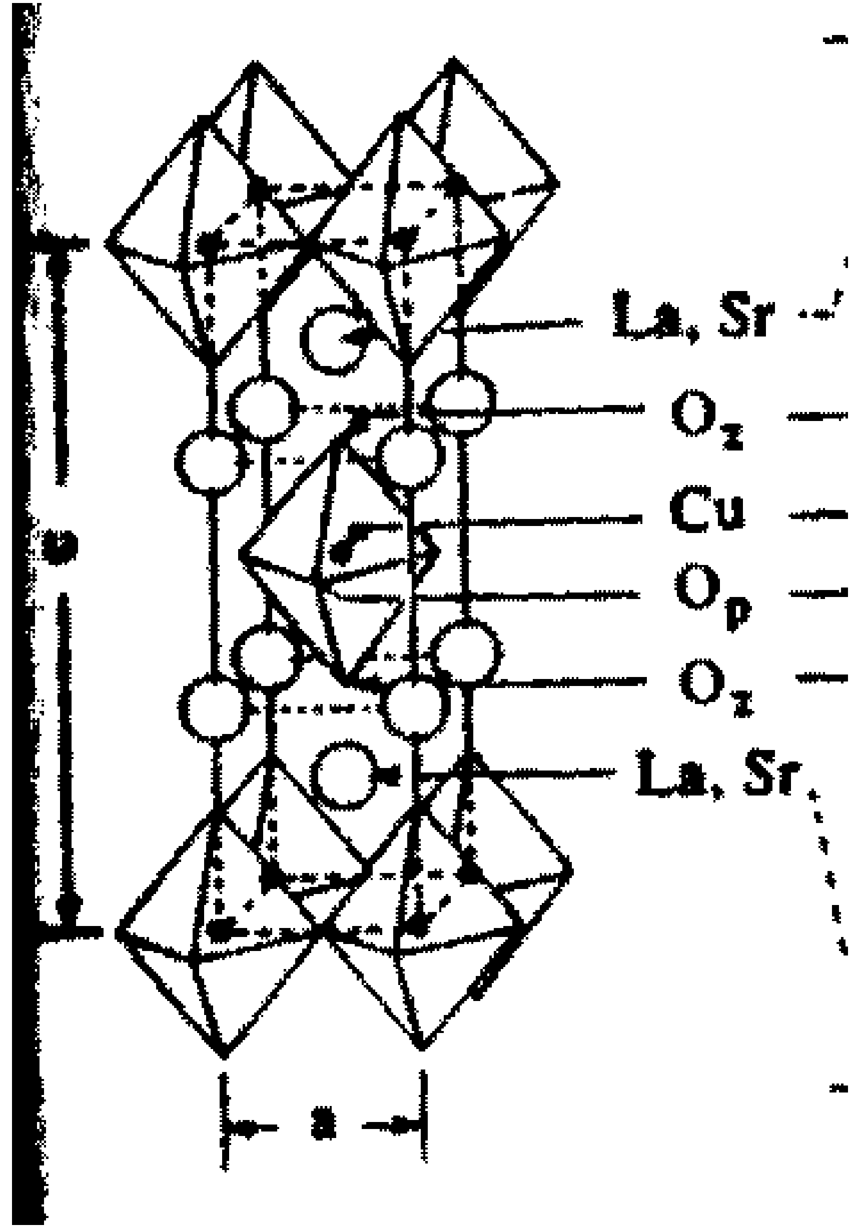
Structure Classes

Structure	Example
21	La_2CuO_4
123	$YBa_2Cu_3O_7$
2201	$Tl_2Ba_2CuO_6$
2212	$Tl_2Ba_2CaCu_2O_8$
2223	$Tl_2Ba_2Ca_2Cu_3O_{10}$
1201	$TlBa_2CuO_5$
1212	$TlBa_2CaCu_2O_7$
1223	$TlBa_2Ca_2Cu_3O_9$
1234	$TlBa_2Ca_3Cu_4O_{11}$

Mostly tetragonal or near tetragonal systems (e.g. tetragonal w/ minor orthorhombic distortions)

re

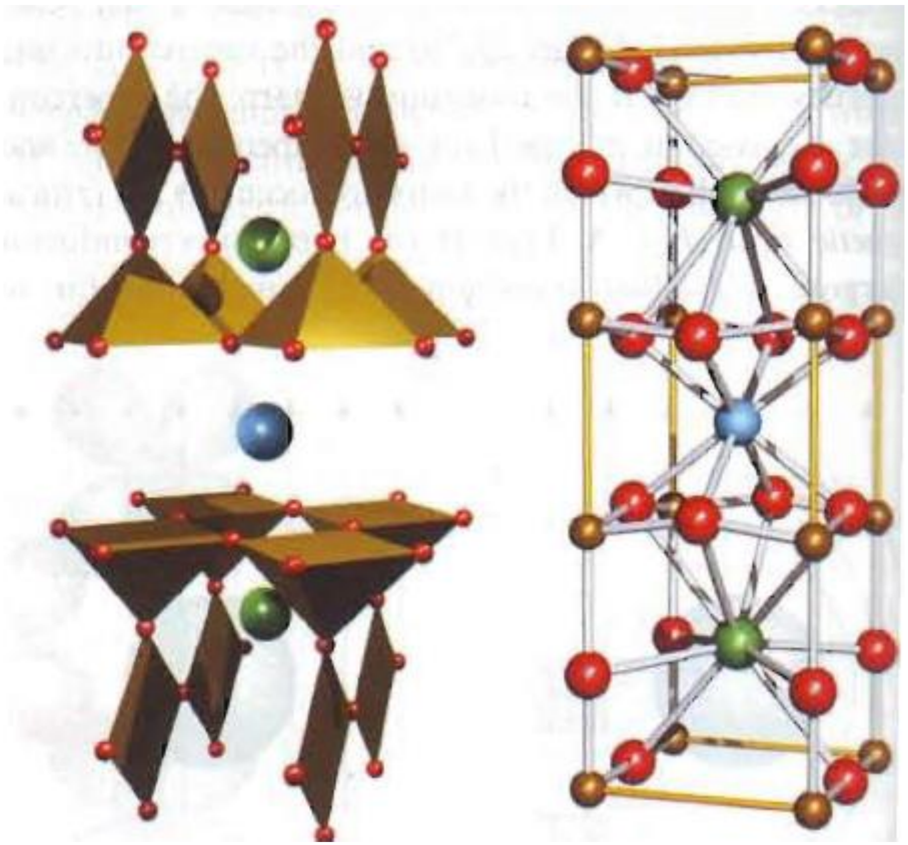
- Perovskite-like
- La is doped often with Sr → $(La_{2-x}Sr_x)CuO_{4-\delta}$
- x = 0 is insulator
- Note the Jahn-Teller Distortion on Cu



$(La_{2-x}Sr_x)CuO_{4-\delta}$

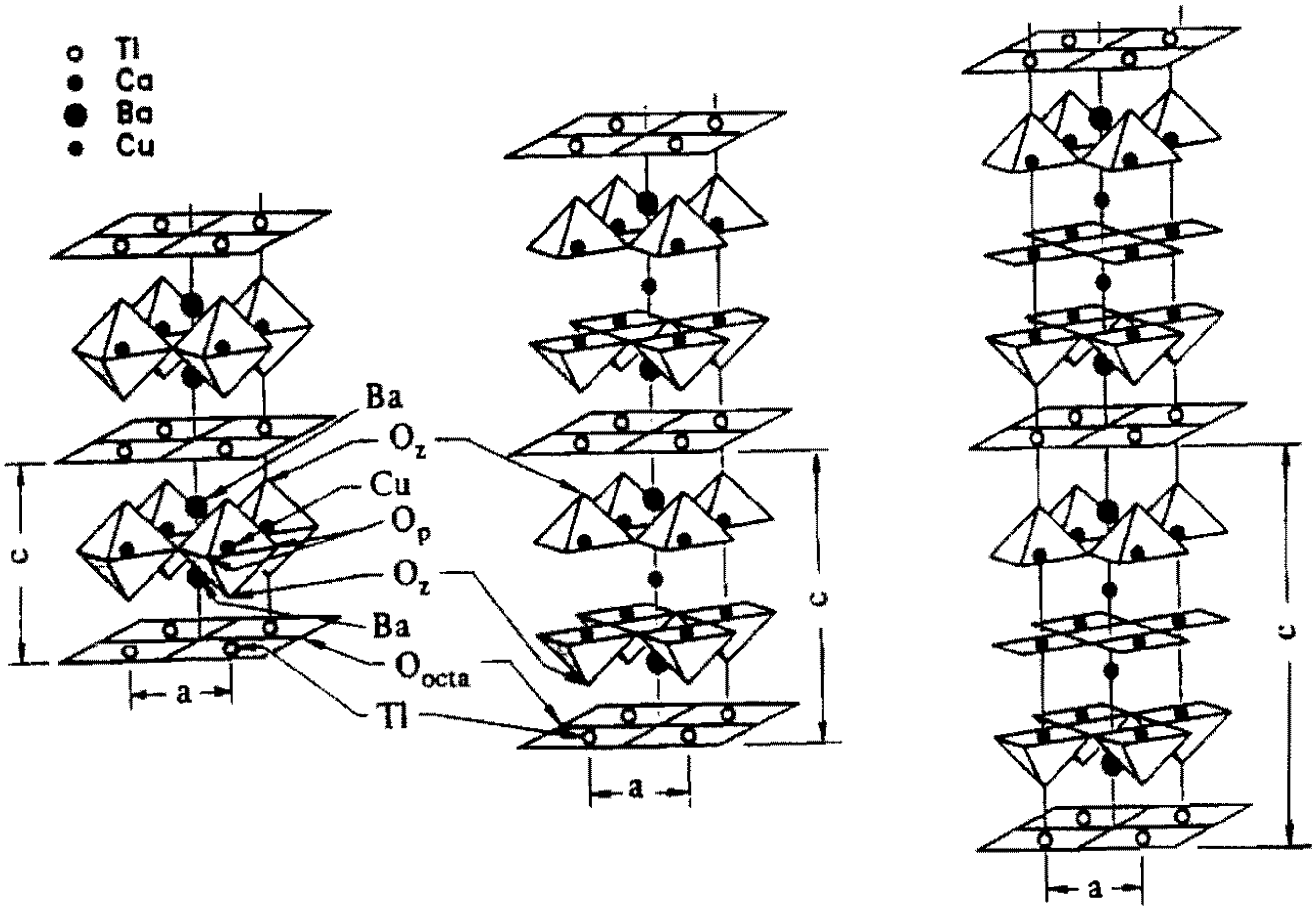
Burns, Gerald. High-Temperature Superconductivity: An Introduction

123 Structure



$YBa_2Cu_3O_7$

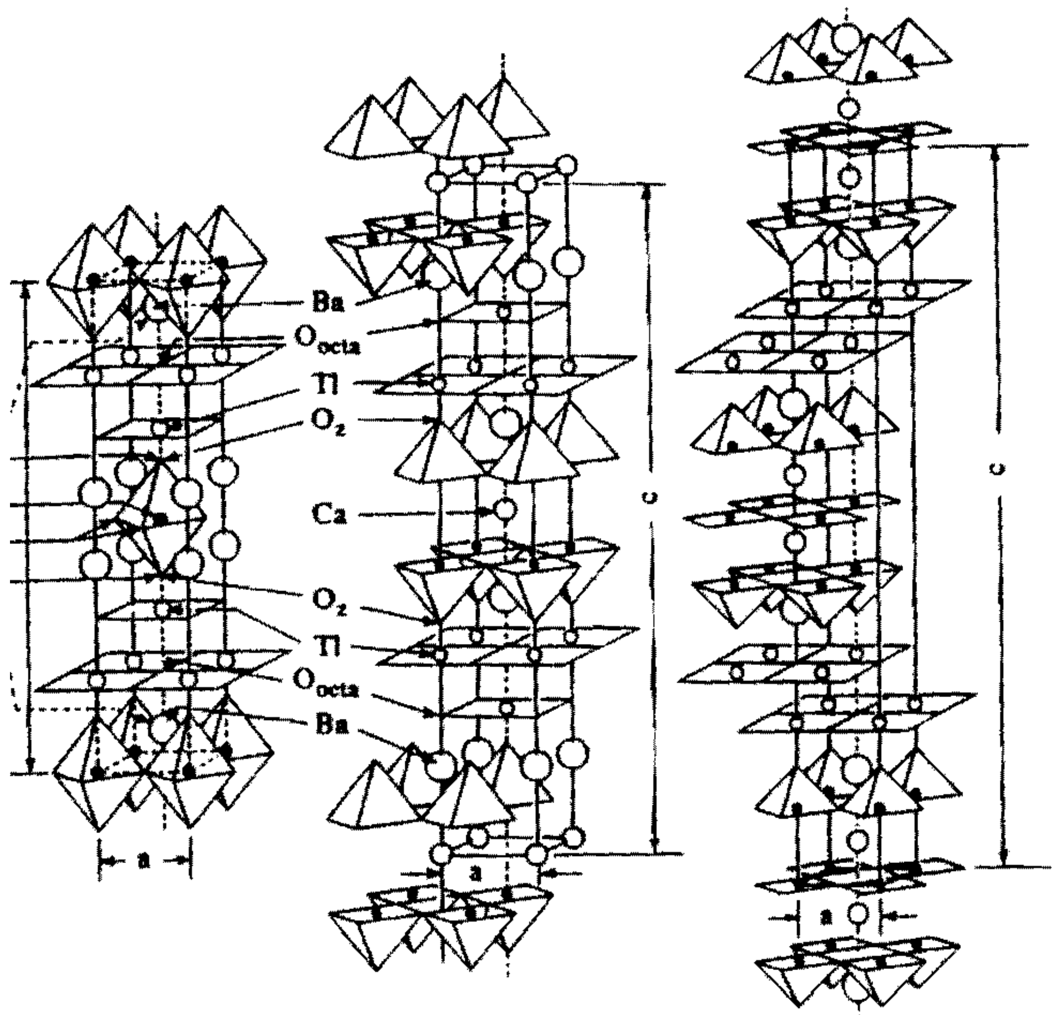
1201 Structural Family



$TlBa_2CuO_5$	$TlBa_2CaCu_2O_7$	$TlBa_2Ca_2Cu_3O_9$	$TlBa_2Ca_3Cu_4O_{11}$
1201	1212	1223	1234

Burns, Gerald. <u>High-Temperature Superconductivity: An Introduction</u>

2201 Structural Family



$Tl_2Ba_2CuO_6$ $Tl_2Ba_2CaCu_2O_8$ $Tl_2Ba_2Ca_2Cu_3O_{10}$

Note octahedral, square pyramidal, and square planar environment of Cu

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Structural Influence on T_c

n	Formula	T_c (K)
1	$Tl_2Ba_2CuO_6$	0-80
2	$Tl_2Ba_2CaCu_2O_8$	108
3	$Tl_2Ba_2Ca_2Cu_3O_{10}$	125

n	Formula	T_c (K)
1	$TlBa_2CuO_5$	0-50
2	$TlBa_2CaCu_2O_7$	80
3	$TlBa_2Ca_2Cu_3O_9$	110
4	$TlBa_2Ca_3Cu_4O_{11}$	122

Greater n = larger T_c

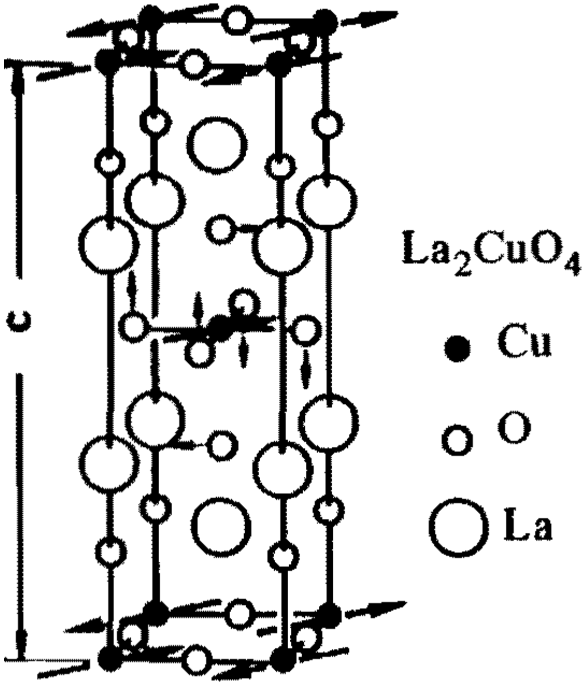
Burns, Gerald. High-Temperature Superconductivity: An Introduction

Transition Types

- Turns from metal to superconductor
  - When $T < T_c$
- Turns from Paramagnetic - Antiferromagnetic
  - When $T < T_N$ (Néel Temperature)
- Phase Transition: Tetragonal - Orthorhombic
  - Makes $b \neq a$

Transitions

- Large black arrows are spin directions below T_N - antiferromagnet
- Small arrows show tilting that cause minor orthorhombic distortions

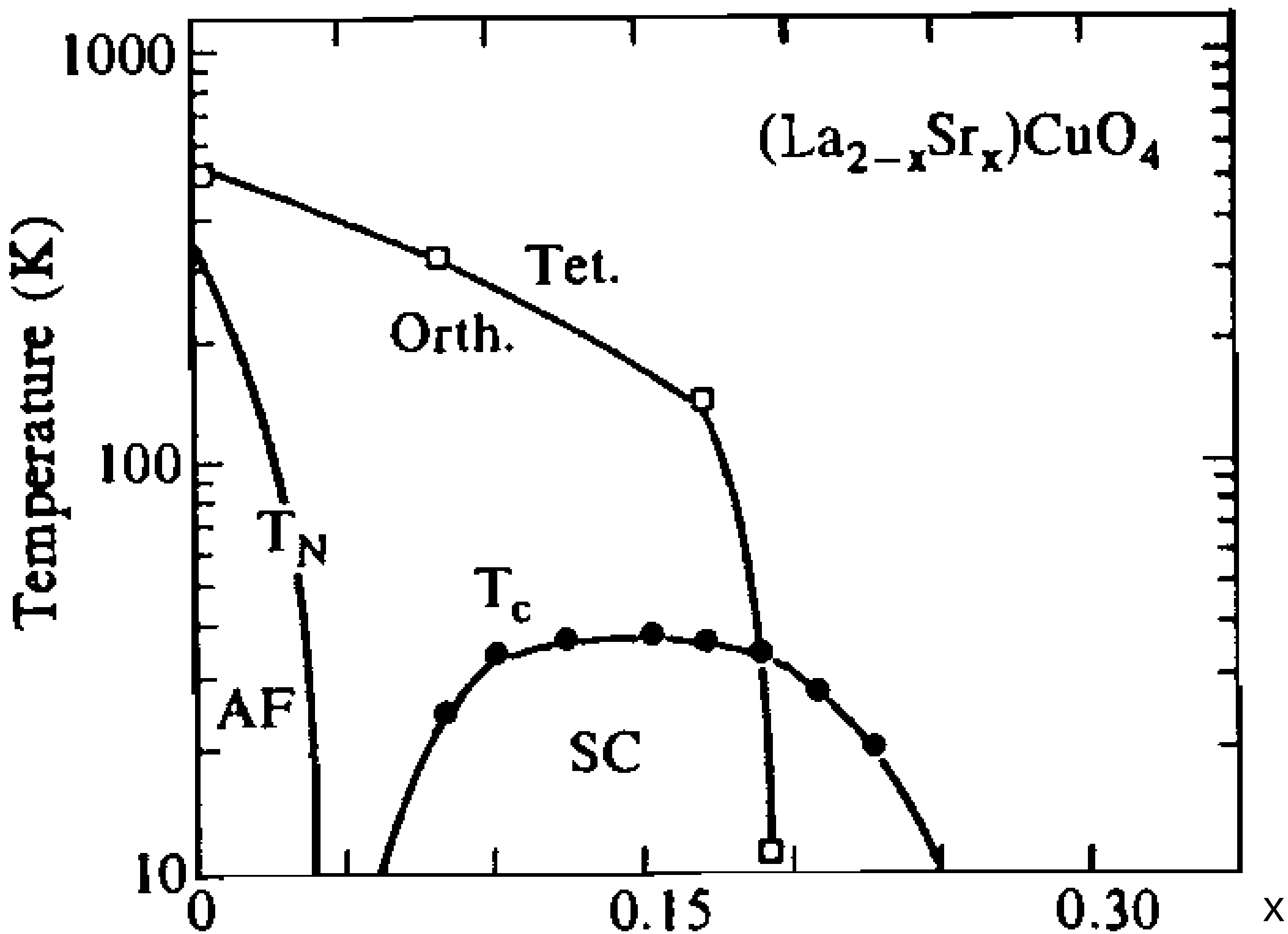


$(La_{1-x}Ba_x)_2CuO_{4-\delta}$

x	a = b (tet)	a (orth)	b (orth)	c (tet)	c (orth)
0.075	3.787	3.798	3.803	13.31	13.234
0.1	3.791	3.786	3.824	13.35	13.234

Burns, Gerald. High-Temperature Superconductivity: An Introduction

Phase Diagram



Burns, Gerald. High-Temperature Superconductivity: An Introduction