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EXPERIMENTAL WORKSHOP ON
"HIGH TEMPERATURE SUPERCONDUCTORS"
(30 March - 14 April 1989)

PREPARATION AND CHARACTERIZATION OF HIGH T_c SUPERCONDUCTORS

Part I

RE - Cuprates

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Preparation & Characterazation of High Tc Superconductor

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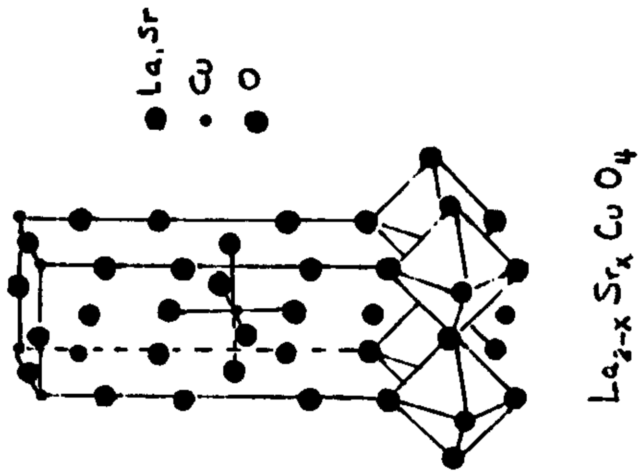
What are high T_c superconductors?

- RE - cuprates

1. $La_{2-x} M_x Cu O_{4+\delta}$ (M = Ba, Sr, Ca) phases
   K_2NiF_4 type structure
   T_c = 30K ~ 40K
   (Beddnotz & Müller)

2. $R Ba_2 Cu_3 O_{7-\delta}$ phases
   R = Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Lu
   except Ce, Pr, Tb
   Layered Perovskite
   T_c = 90K
   (Wu & Chu)

3. $R Ba_2 Cu_4 O_8$ (R = Y, La, ...) &
   $R_2 Ba_4 Cu_7 O_{15}$ (R = Y, Yb)
   Both can be considered as intergrowth in $Y Ba_2 Cu_3 O_7$.
   T_c = 40 ~ 86 K



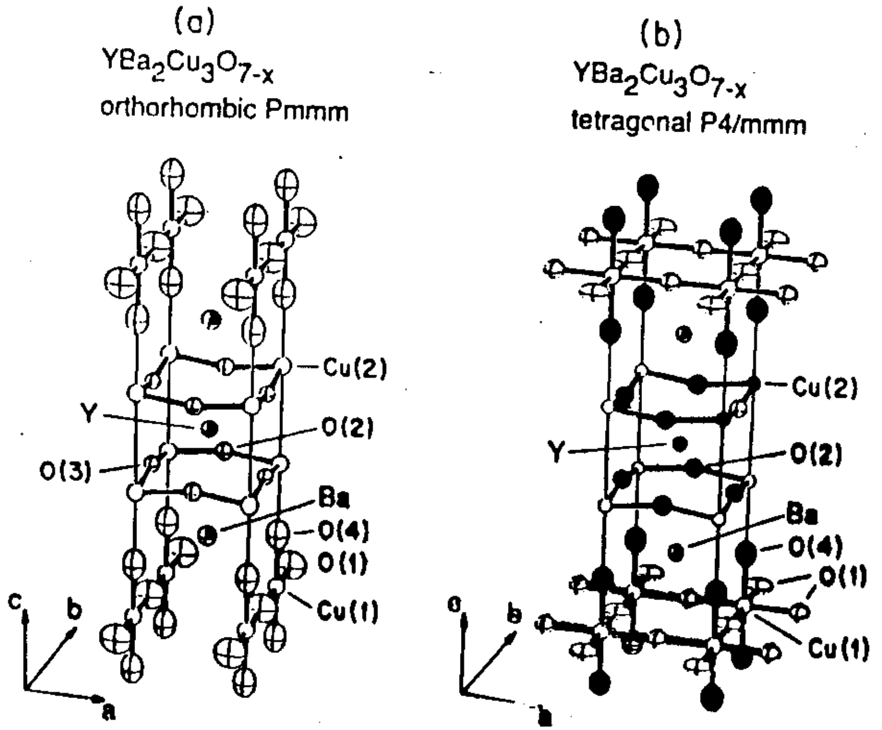


FIG. 1. Structures of the (a) orthorhombic (*Pmmm*) and (b) tetragonal (*P4/mmm*) phases of $YBa_2Cu_3O_{7-x}$. Note that the oxygen atoms in the plane at $z=0$ are disordered in the tetragonal phase.

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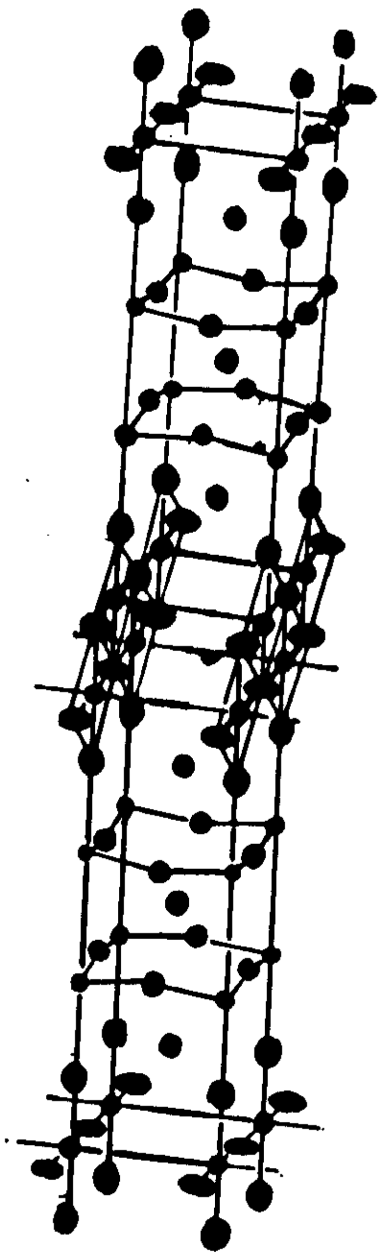

* $Y_2Ba_4Cu_8O_{16}$

$= 2\ YBa_2Cu_3O_7$

$+ 2\ CuO$

* Double chain share eadge.

4. Bi -, Pb -, Tl - cuprates:

Many of most recently discovered superconductors may be represented as

$$A_m M_2 Ca_{n-1} Cu_n O_{2n+m+2} \quad (m = 1, 2 \; ; \; n = 1, 2, 3, 4)$$

where: M = Ba, Sr.

Cation A = Bi, Tl, Pb, a mixture of Bi & Pb, Bi & Tl, Tl & Pb.

* Ca can be partially substituted by Sr or Y.

Ex: $Pb_2 Sr_2 Ca_{.5} Y_{.5} Cu_3 O_{8+\delta}$ (T_c = 70K)

$Pb_2 Sr_{2-x} Ca_x Cu_3 O_{8+\delta}$

* All of them have very similar structure,

Rock Salt + Layered Perovskite

* The structure contains n Cu-O sheets
* T_c = 12K ~ 125 K.
* Doping Antimony (Sb) in $(Bi, Pb)_2 Sr_2 Ca_2 Cu_3 O_{10}$

UCST reported:

$Bi_{1.7} Pb_{.2} Sb_{.1} Sr_2 Ca_2 Cu_3 O_{10+\delta}$

T_c = 130K or higher ?

It's not stable & hard to reproduce.

In China, no body can repeat their results except themselves.

Only using very small measuring current (10 μA), you can observe the same thing ?

5. n - type superconductors: (electrons are charge carrier)

$R_{2-x} M_x Cu O_{4-y}$ (x = .15) T_c = 20K

Table 2. Summary for $(AO)_m M_2Ca_{n-1}Cu_nO_{2n+2}$ phases.

Compound	a(Å)	c(Å)	T_c(K)
$TlBa_2CuO_5$	3.83	9.55	*
$TlBa_2CaCu_2O_7$	3.833	12.68	90
$TlBa_2Ca_2Cu_3O_9$	3.853	15.91	110
$TlBa_2Ca_3Cu_4O_{11}$	3.850	19.01	122
$(Tl,Bi)Sr_2CuO_5$	3.745	9.00	50
$(Tl,Bi)Sr_2CaCu_2O_7$	3.800	12.07	90
$(Tl,Pb)Sr_2CaCu_2O_7$	3.800	12.15	90
$(Tl,Pb)Sr_2Ca_2Cu_3O_9$	3.808	15.23	122
$Tl_2Ba_2CuO_6$	3.866	23.24	90
$Tl_2Ba_2CaCu_2O_8$	3.855	29.42	110
$Tl_2Ba_2Ca_2Cu_3O_{10}$	3.849	35.66	122
$Bi_2Sr_2CuO_6$	3.796	24.62	12
$Bi_2Sr_2CaCu_2O_8$†	3.823	30.90	90
$Bi_2Sr_2Ca_2Cu_3O_{10}$†	3.818	37.88	110

*Not superconducting. †Cell dimensions are for an idealized subcell.

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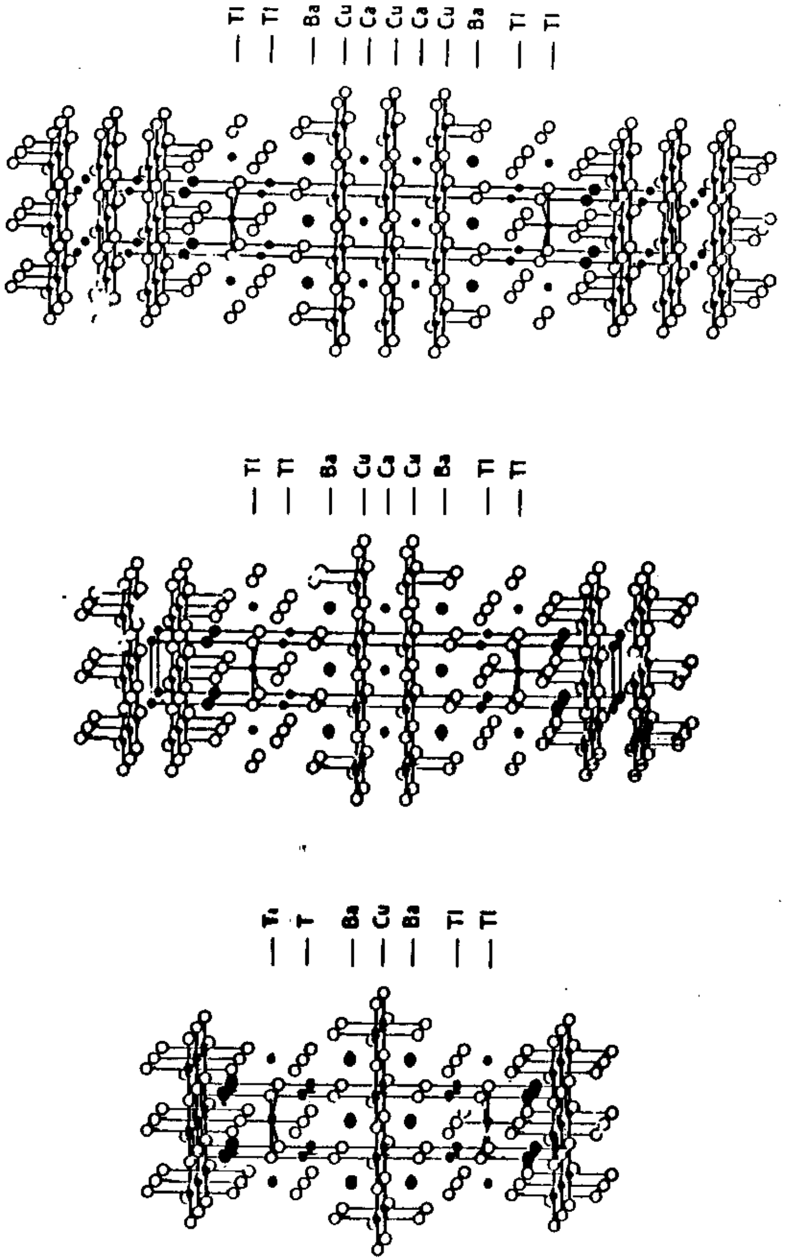

Fig. 5. The structures of [illegible] for n = 1, 2, and 3.

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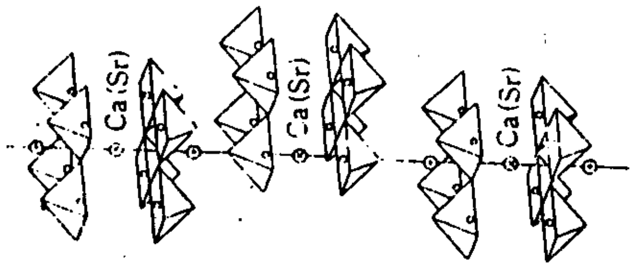
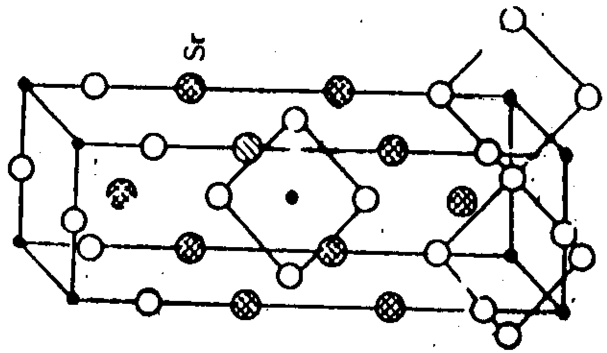
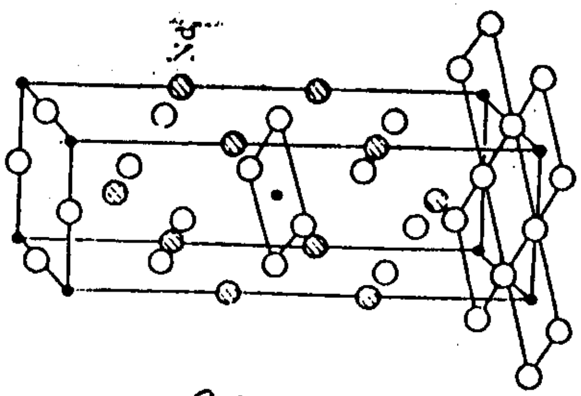
Compounds	Lattice parameters		T_c
$Pb_2Sr_2YCu_3O_8$	a = 5.40, b = 5.43,	c = 15.74	—
$Pb_2Sr_2Ca_{1-x}Y_xCu_3O_{8+\delta}$ (.2 ≤ x ≤ 1.2)			79K
$PbBaSrYCu_3O_8$	a = 3.84,	c = 27.66	—
$BiPbSr_2YCu_2O_8$			—
* $Bi_2Sr_{3-x}Y_xCu_2O_y$ (x > .3)			70K
* $Bi_2Sr_{2-x}Pb_xYCu_2O_{8+y}$ (x ≥ .2)			70K
* $Bi_2Sr_{2-x}Na_xYCu_2O_{8+y}$ .2 ≤ x < .5			70K
$Bi_2Sr_2CuMnO_y$			—
$Bi_2Sr_2Fe_2O_y$	a = 3.85,	c = 31.6 (2212)	—
$Bi_2Sr_2CoO_y$			—
$Bi_2Sr_2Co_2O_y$	a = 3.85,	c = 29.8	—
$(Tl_{.5}Pb_{.5})Sr_2CaCu_2O_7$	a = 3.80,	c = 12.05	80 - 90K
$(Tl_{.5}Pb_{.5})Sr_2Ca_2Cu_3O_{10}$	a = 3.81,	c = 15.23	115 - 122K
* $(Tl_{.5}Pb_{.5})_2Sr_2Ca_2Cu_3O_{12}$			≥100K
$TlSr_2Ca_{1-x}R_xCu_2O_7$ (R = Er, La, Sm)			40 ~ 70K
$Tl_{1-x}Pb_xSr_{2-y}Pr_yCuO_5$			70K
$Tl_{.5}Pr_{1.5}Sr_{1.5}CuO_5$			—
$La_2SrCu_2O_6$	a = 3.85	c = 19.86	—
$La_{2-x}Sr_xCaCu_2O_6$			?
$Pr_2NiO_{4.2}$	a = 5.487,	c = 12.507	
Ba_2CuO_{3-x}	a = 5.64,	c = 12.97	
$Ba_{25}Cu_{22}O_{50-x}$	a = 17.14,	c = 9.29 (Tet.)	
$Ba_{88}Cu_{96}O_{185}Cl_2$	a = 18.28	(cubic)	



(c) $La_2SrCu_2O_6$, $La_2CaCu_2O_6$ $\times(p=0\sim0.25)$ $m=2$



(c) Sr_2CuO_3



(b) Nd_2CuO_4

R = Pr, Nd, Sm, M = Ca^{4+}, Th^{4+}

* Nd_2CuO_4 type structure differs from K_2NiF_4 Cu atom is surrounded only by a squar planner Oxyg not octahedral coordination.

* Oxygen conten is less than 4, $y \sim x$ 0.01 - 0.03

* higher T_c exists in n-type superconductors ?
T_c = 85K in mixed phase materials of nominal composition $Tl_{2.2}Ba_2CaCu_3O_x$. ?

- Bismuthates: $BaPb_{1-x}Bi_xO_3$ (x ~ 0.3)
  $Ba_{1-x}K_xBiO_3$ (x ~ 0.35 - 0.4)
  T_c ≈ 30K, Cubic perovskite
  3D superconductor, not 2D.

Main experimental results:

- Structural:

1. Layered perovskite:
   Most of SC have 2D crystallographic & electronic structure. CuO_2 plane plays important role. It is necessary for high T_c ?
   Ex: $La_2SrCu_2O_{6+\delta}$ has the stacked Cu-O sheets, but nonsuperconducting.
   (Synthesis condition: 1100°c, 2k bar oxygen)

2. T_c varies with doping oxygen concentration. So, it is sensitive to partial oxygen pressure.
   Ex: $La_2CuO_4 \longrightarrow La_2CuO_{4+\delta}$
   $YBa_2Cu_3O_{6.4} \rightarrow YBa_2Cu_3O_{7.0}$

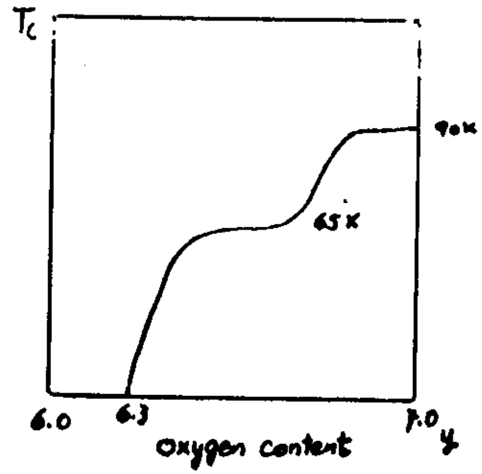
For YBCO, oxygen content increasing from 6.4 to 7.0.
T_c increases, and has two plateaus (60K & 90K)

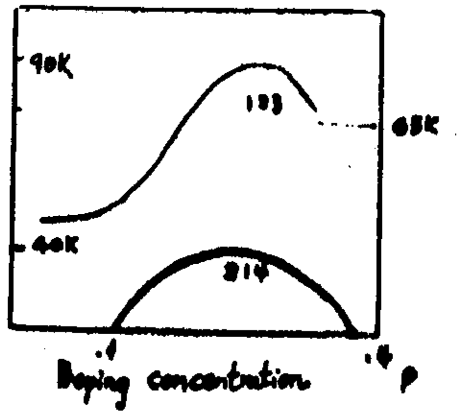
3. For $RBa_2Cu_3O_{7-\delta}$, R substitution does not change T_c, but changes c parameters.
4. For $R_{2-x}M_xCuO_4$ & $Ba_{1-x}K_xBiO_3$ type compounds, T_c increases; when doping concentration increases at lower doping concentration, then T_c saturates and decreases with a further increasing of doping concentration.
5. Any substitution for Cu, either on chain or on plane, lower T_c and decreases χ.
6. T_c increases when c parameter increase, then T_c decrease with the further increasing c.

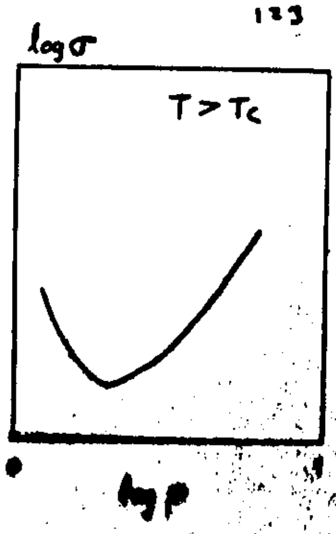
• Physical:

1. Isotope effect: O^{18} substitutes for O^{16}. T_c shifts.
   $\alpha = 0.2$ in LSCO
   $\alpha = 0.0$ in YBCO
   $\alpha = 0.45$ in BKB. (BCS)
   * Los almos give different results for YBCO.
2. Specific heat,
   For YBCO, small jump at T_c. Linear term below T_c, & upturn at very low temperature ?
   For LSCO, Bi- & Tl- cuprate, No obvious jump at T_c
3. Spectrum measurement (Inelastic, Neutron scattering, IR, RS, NMR, μSR)
   Δ exists, $2\Delta/kT_c \approx 7-8$ for YBCO
   $2\Delta/kT_c \approx 3.6$ for BKB & LSCO.

μSR: $T_c \propto n_s/m^*$







4. Elastic moduli. Vsound jump at T_c
5. Anisotropic behavior of Resistivity & Magnetic moment. along c & perparticular c axis.
6. Succeptibility χ are not much different for SC and NON SC at $T > T_c$.

$YBa_2Cu_3O_{7-\delta}$ preparation:

- Solid state reaction
- Starting Materials: Y_2O_3, $BaCO_3$, & CuO powders.
- Powders were mixed and ground, pressed into pellets.
- Fired at 940°C – 950°C for 24h. in flowing O_2, then furnace-cooled in air.
- Reground and Screened (200 mesh), pressed into pellets.
- Reheated at 940°C for 24h in air.
- Cooled down to 520°C (below tetragonal → Orthorohmbic phase transition temperature) and held for 24h.
- Furnace-cooled to RT in 6h.

Generally, the synthesis of superconducting $YBa_2Cu_3O_{7-\delta}$ requires two steps,

First, $YBa_2Cu_3O_{6+x}$ with tetragonal symmetry is formed.

Second, Oxidation to $YBa_2Cu_3O_{7-\delta}$ with Orthorohmbic symmetry is carried out at a low temperature.

When Oxygen diffuses into $YBa_2Cu_3O_{6+\delta}$ to reform $YBa_2Cu_3O_{7-\delta}$, this change causes defects such as twins, stacking faults, strain, microcracks, domains, and lower specimen desity.

Usually, Jc is low.

One step synthesis of superconducting 123 phase at low temperature is really needed.

Charaterazation:

1. T_c : 90K – 95K, from Resistance & Susceptibility measurements.
2. Orthorohmbic triple layered perovskite from X-ray diffraction (≯ 1% intensity)

\# T_c varies with quenching temperature

\# T_c changes with oxygen pressure.

Ex. Under the high oxygen pressure, the oxygen content might go beyond 7.0, but bulk $YBa_2Cu_3O_8$ is not layered perovskite and non superconducting.

Substitution work:

So far, there are too much substitution work.
I summerize here briefly, It should satisfy:

1. Keeping the same structure, sometimes it is necessary to keep superconductivity.
2. true composition is clear, know the true occupied site.
3. Obtain single phase, not multiple-phases.

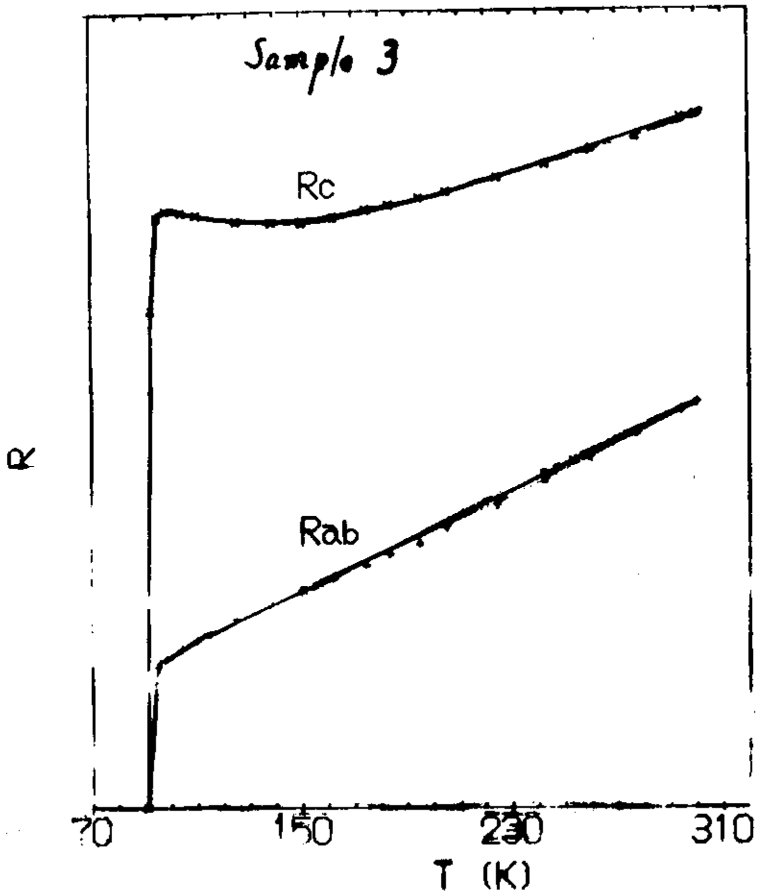
Now, the main results of substitutions work are listed here.

\# None have increase T_c

\# For Y, Most of RE can substitute for Y, except Ce, Pr, Tb

Ex: $PrBa_2Cu_3O_7$ isostructural to $YBa_2Cu_3O_{7-\delta}$, but non-superconducting.

Anisotropic resistivity vs temperature curves of the small single crystal.



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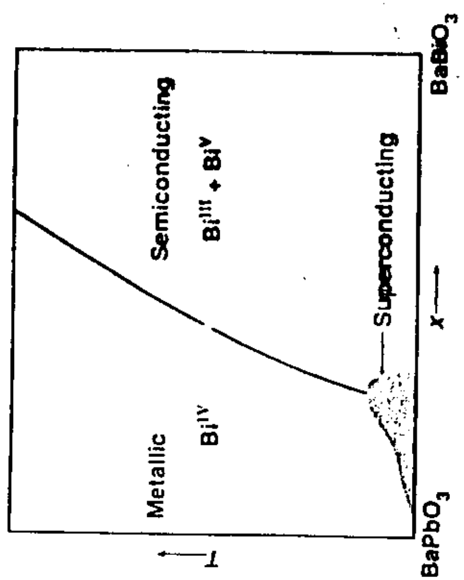


Fig. 7. Schematic phase diagram for $BaPb_{1-x}Bi_xO_3$. Vertical axis is temperature.

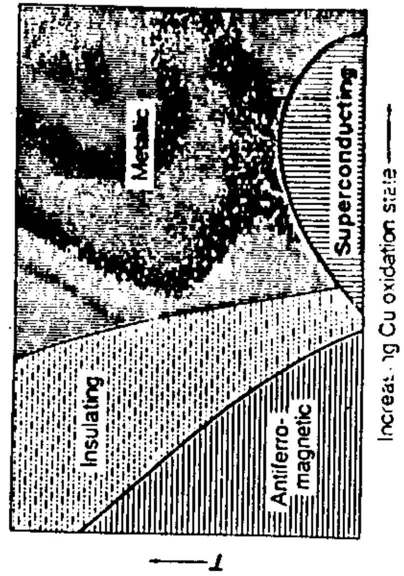


Fig. 8. Antiferromagnetism and superconductivity for $La_{2-x}A_xCuO_4$, $YBa_2Cu_3O_{6+x}$ and $Bi_2Sr_{3-x}Y_xCu_2O_8$ systems. Vertical axis is temperature.

Sleight et al.

For Ba & Cu,

Tc always drops and ultimately sc disappears.

For Oxygen, F can push up Tc ?

• $Nd_{2-x}Ce_xCuO_{4-y}$ (x=0.15, y=0.02) (Tokura et al)

New n-type superconductor. T_c = 15 ~ 20K.

Doping Ce^{4+} in non superconducting Nd_2CuO_4.

* Normal state resistivity changes when doping concentration increases.(x).

x = 0.15, ρ reaches the minimum point. for Ce doping Nd_2CuO_4. However, for Th^{4+} doping, there is no turn of R vs T curve.

* T_c depends on the Ce concentration (x).

x ≤ 0.15 . superconducting

x > 0.15 . Metallic & non superconducting.

* structure, Nd_2CuO_4 type. tetragonal.

Cu atoms is surrounded only by a square planar array of oxygen atoms, unlike octahedral coordination in La_2CuO_4.

* Oxygen analysis indicates y ranges from 0.01 to 0.02.

* charge carrier: Electrons. supplied by Ce^{4+} ions.

Hall coefficient is negative.

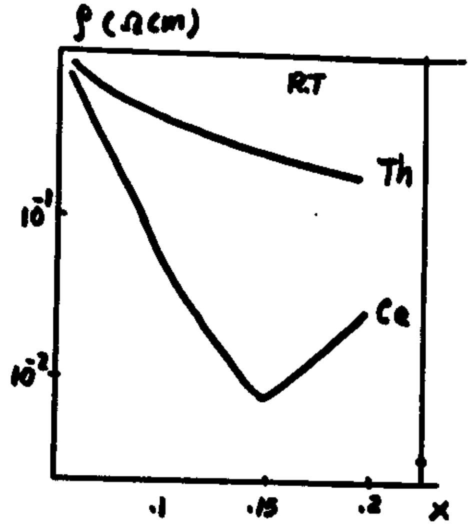
1. preparation;

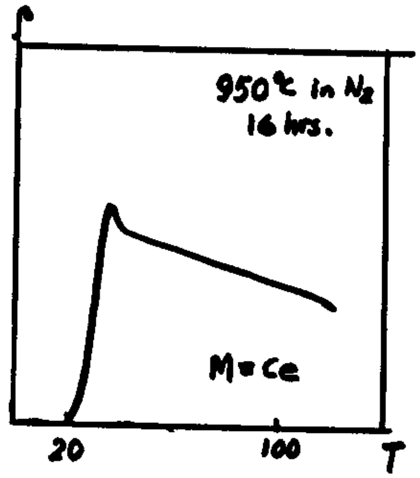
1. stoichiometric mixture of Nd_2O_3, CeO_2 & CuO powders were ground together.

2. Preheated at 900°C in air for 20h (Alumina crucible) or at 950°C for 10h.

3. Reground & fired at 900°C in air for 20h twice.

4. Resulting powders were pressed into pellets.





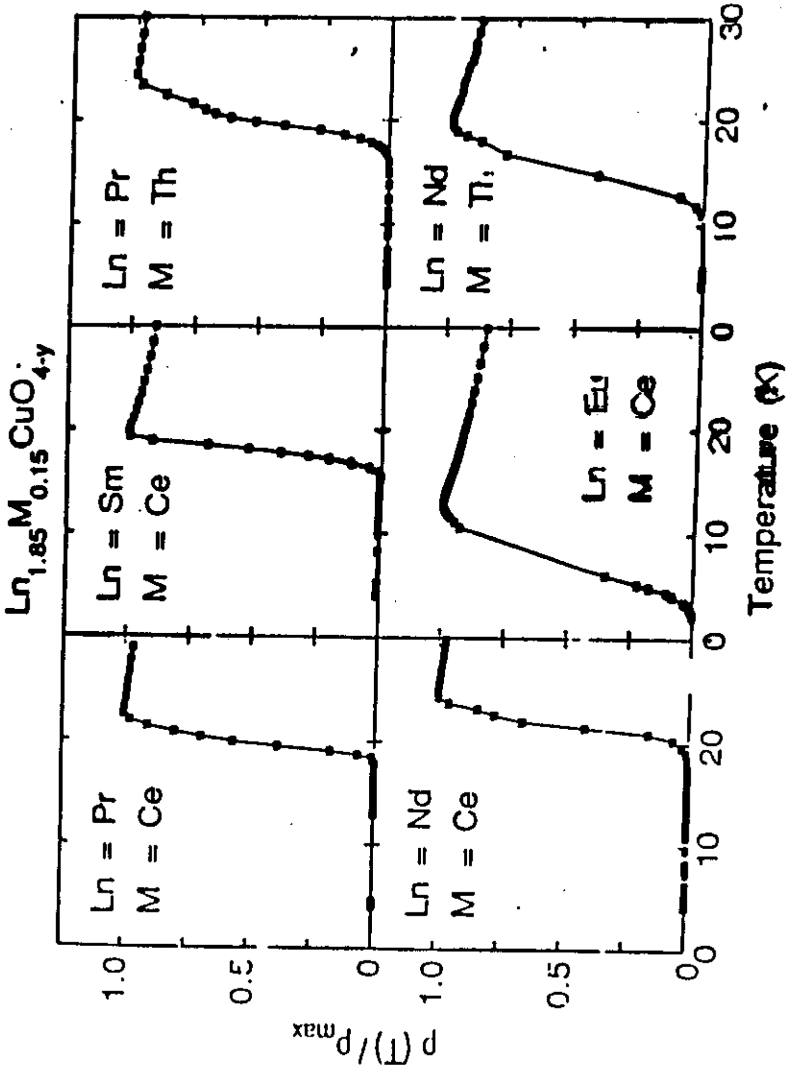


Fig. 4. Normalized electrical resistivity, $\rho(T)/\rho_{max}$, plotted as a function of temperature T over the range $0 \le T \le 30$ K for six $Ln_{1.85}M_{0.15}CuO_{4-y}$ electron superconductors. Data for Ln = Pr, Nd, Sm, and Eu, M = Ce, and Ln = Pr and Nd, M = Th are shown. All samples shown were helium-annealed at temperatures in the range 885–910°C. Considerable variation of T_c with host and dopant ions is evident.

5. sintered at 1100°c in air for 16h.
6. Quenched in air to RT → single phase, T_c = 15K
7. Reduced in flowing N_2 or He at 850°c ~ 950°c for 16h.
   Multyple specimen with T_c ≠ 20K.
   Amount of impurity phase is less than 8 % weight.

Status:

* T_c = 15K ~ 20K (Zero Resistivity temperature)
* 8% ~ 12% meissner effect. small
* structure determined by x-ray diffraction.
  Isomorphous to Nd_2CuO_4
* Oxygen deficience is small y = 0.01 ~ 0.03.
  by Iodometry
* Hall coefficient is negative
  Ce^{4+} supplied charge carrier – Electrons.
* Substitution,
  Ln = Pr, Sm, Nd, Eu.
  M = Ce, Th.
* Superconductivity & AF coexist
  T_N = 1.8K ~ 8K.

Single crystal, large size & high quality
Attempts to find out the higher T_c n-type sc.

Possible Superconducting $La_{2-x}Sr_xNiO_{4+\delta}$ (x = 0.2) ?

Since $La_{2-x}Sr_xCuO_4$ was discovered. Many attempts have been made to synthesize superconducting compounds with S = 1.

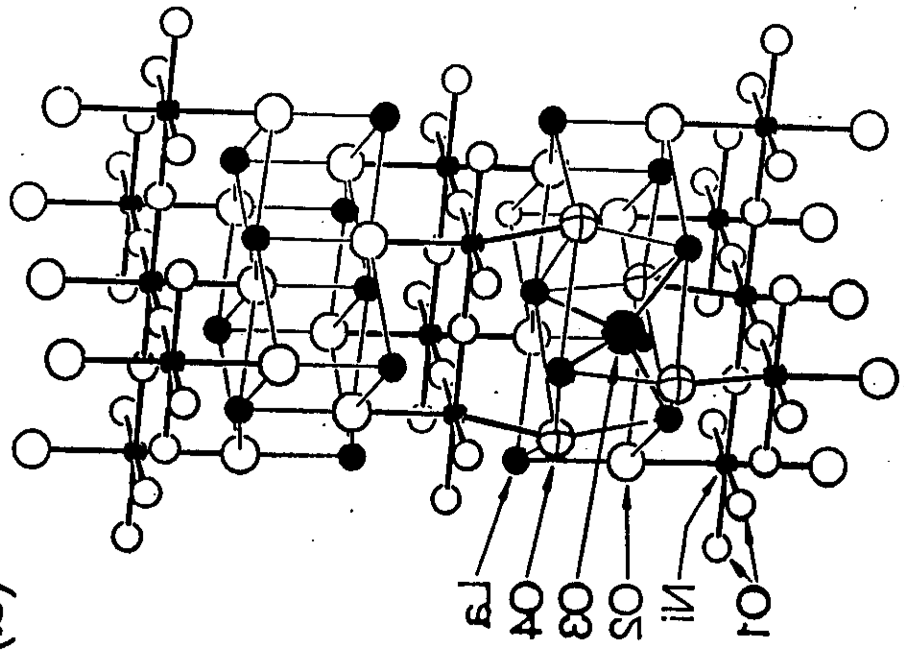
No body was successful in making superconducting Ceramics.

Recently, Purdue University declaimed. They synthesized Superconducting $La_{2-x}Sr_xNiO_4$

1. Preparation: Solid state Reaction does not work.
   - Radio frequence induction skill melting & Bridgeman Method is used to grow single crystal.
     Induction heating to melt materials. T = 1650°C
     Water cooled Cu crygible.
   - Crystals are very hard, isolate small part
   - Low oxygen pressure required for stablizing SC phase

$$-7 \geq \log f_{O_2} \geq -9.$$

2. Structure:
   S.G: Bmab　　　Orthorohmbic
   $\delta = 0$
   Isostructural to $La_{2-x}Sr_xCuO_4$



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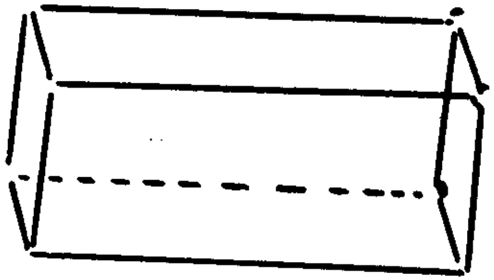


3. Resistivity :

R vs T curve shows a strange behavior,

first strong semiconducting part (RT – 60K)

Second part (60K ~ 40K) : Almost Insulator
Constant current source saturated.

Third part : Metallic & Superconducting
$T_c^{Zero} \approx 19K$.

4. A. C. Magnetic Susceptibility.

χ vs T curve is also strange.

- very slow cooling rate is necessary.
  3h from RT to LN_2

- At least 3 cycles from RT to 4.2K.
  $T_c^{onset} \approx 75$ K.
  ?

- Several cooling – heating cycles from RT to 4.2
  T_c disappears
  ?

5. χ (T) does not saturated until 15 kOe.

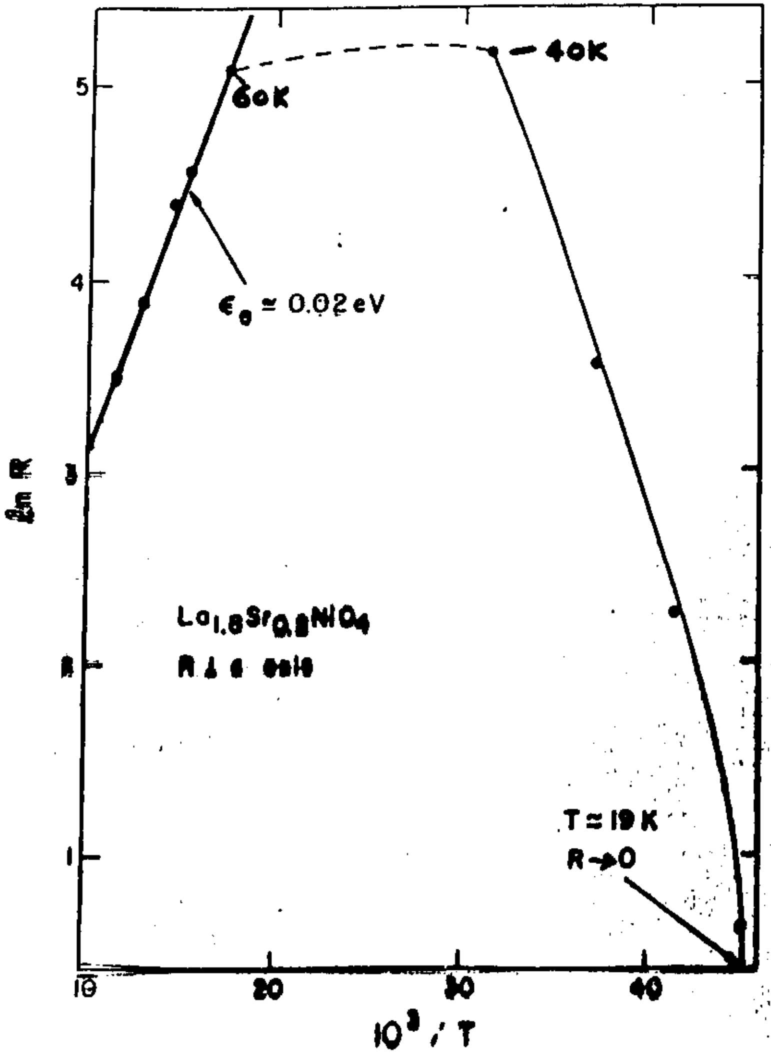
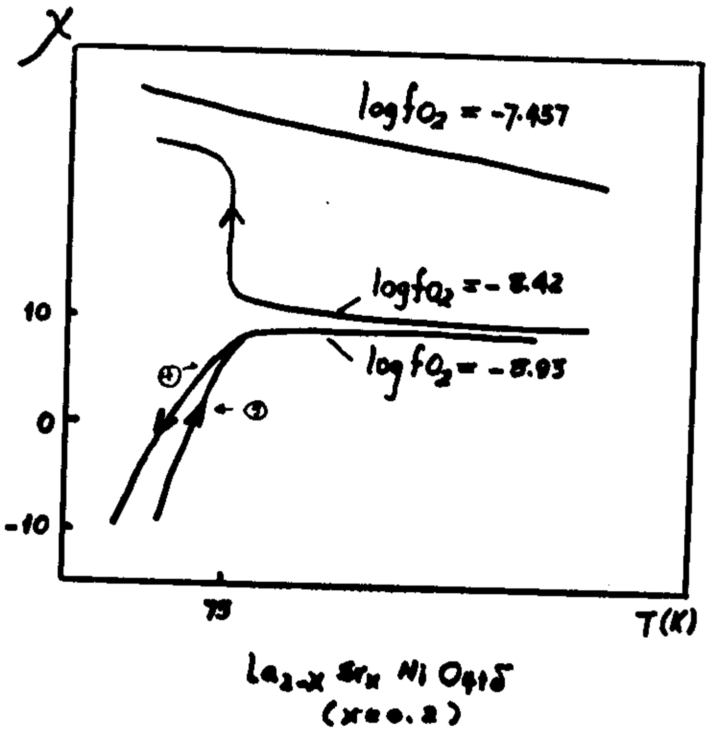


Fig 3 [illegible] J. Spalek, Z. [illegible] [illegible] Honig



Different partial oxygen pressure

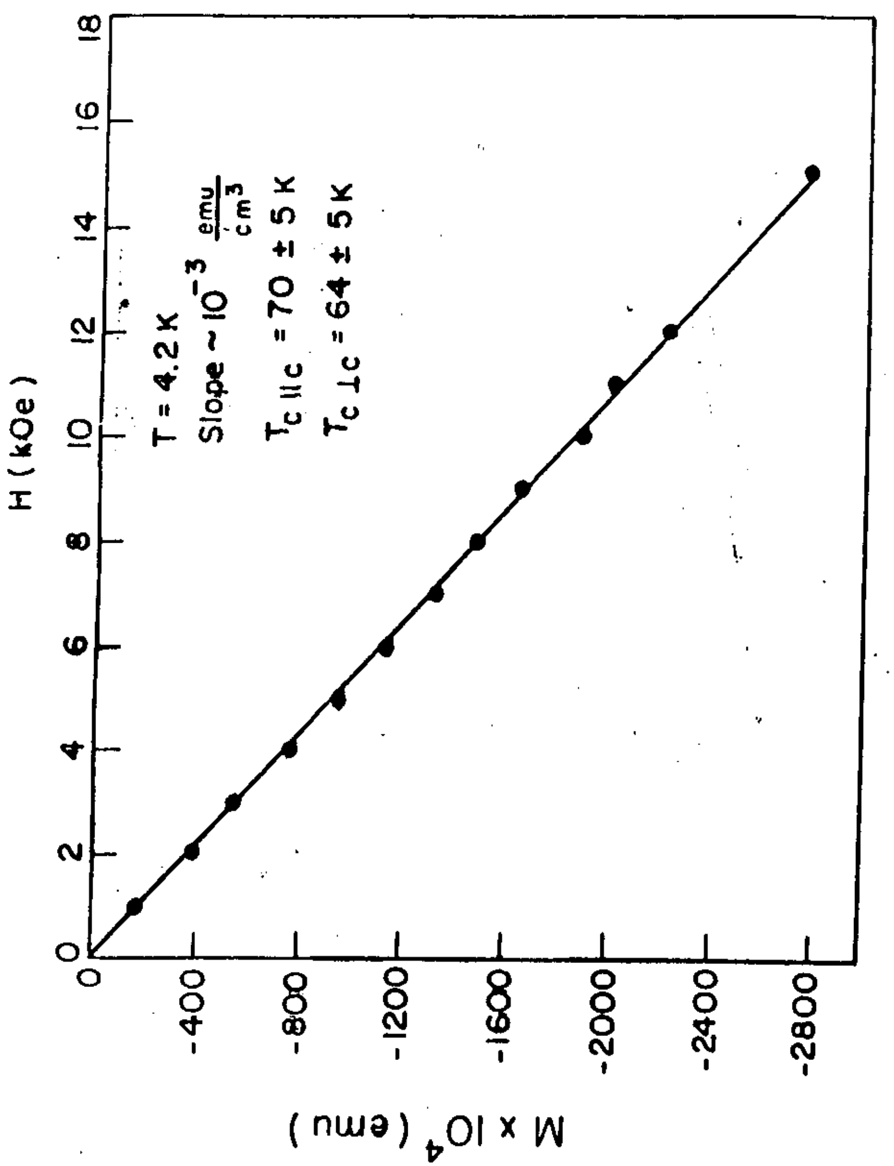


Fig. 2 (J. Spalek , Z. Fisk J. H. H..