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EXPERIMENTAL WORKSHOP ON HIGH TEMPERATURE SUPERCONDUCTORS & RELATED MATERIALS
(BASIC ACTIVITIES)

12 - 30 MARCH 1990

HTSC SYNTHESIS & PROCESS

PART III

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(V) The other s.c-ing compounds and Related Materials.

1. So far, many new family of s.c were discovered. The main results are listed in the table.

	compounds	Lattice parameters (Å)	T_c
1.	$Pb_2 Sr_2 Y Cu_3 O_8$	a = 5.40, b = 5.43, c = 15.74	–
2.	$Pb_2 Sr_2 Nd Cu_3 O_8$	a = 5.435, b = 5.463, c = 15.817	–
3.	$Pb_2 Sr_{2.24} Nd_{.76} Cu_3 O_8$		70K
4.	$Pb Ba Sr Y Cu_3 O_8$	a = 3.84, c = 27.66	–
5.	$Pb_2 Sr_2 Ca_{2-x} Y_x Cu_3 O_{8+\delta}$ $(0.2 \leq x \leq 1.2)$	–	79K
6.	$Bi Pb Sr_2 Y Cu_2 O_8$	–	–
7.	$Bi_2 Sr_{3-x} Y_x Cu_2 O_7$ $(x > 0.3)$		70K
8.	$Bi_2 Sr_{2-x} Pb_x Y Cu_2 O_{8+y}$ $(x \geq 0.2)$		70K
9.	$Bi_2 Sr_{2-x} Na_x Y Cu_2 O_{8+y}$ $(.25 < x < .5)$		70K
10.	$(Tl_{.5} Pb_{.5}) Sr_2 Ca Cu_2 O_7$	a = 3.80 c = 12.05	80-90K
11.	$(Tl_{.5} Pb_{.5}) Sr_2 Ca_2 Cu_3 O_{10}$	a = 3.81, c = 15.23	115-120K
12.	$(Tl_{.5} Pb_{.5})_2 Sr_2 Ca_2 Cu_3 O_{13}$		≥ 100K
13.	$Tl Sr_2 Ca_{1-x} R_x Cu_2 O_7$ (R = La, Nd, Er, Sm)		70K
14.	$Tl_{1-x} Pb_x Sr_{2-y} Pr_y Cu O_5$		70K
15.	$(Y_{1-x} R_x)(Ba_{2-y} R_y) Cu_3 O_{7-\delta}$		~60K
16.	$Bi_2 Sr_3 Fe_2 O_y$	a = 3.88, c = 31.6	—
17.	$Bi_2 Sr_2 Co O_y$		—
18	$Bi_2 Sr_3 Co_2 O_y$	a = 3.85, c = 29.8	—
19.	$La_2 Sr Cu_2 O_6$	a = 3.85, c = 19.36	—
20.	$Sr_2 Cu O_3$		—

what in the next new s.c ? where can we find out it ?

2. common characteristics of All superconductors :

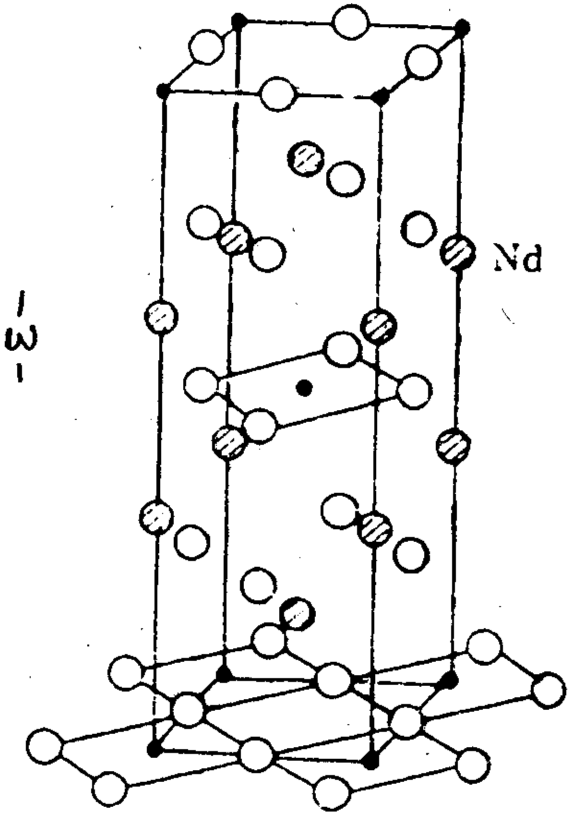
- Components of s.c are getting more and more :
  up to 5 different elements (only for cations)
- Structures are becoming more and more complicated.
  Cations Sublattice with a longer period along $\bar{c}$ direction.
  I modulation, as well as various imperfections.
- All have only orthombic or tetragonal symmetry except
  Cubic symmetry (BKB)

- All structures can be derived from the perovskite structure.
  The spinnel and other type structure
  didn't work, so far.

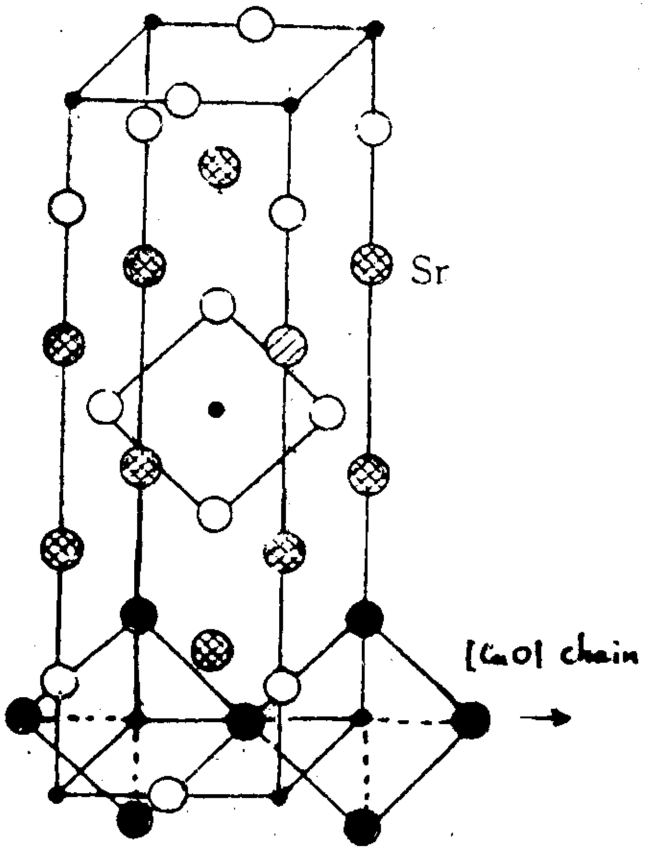
- All have the oxygen deficiency —— defect perovskite.
  oxygen - to - metal ratios < 1.5
  ⇒ It's hard to form the three - dimensional framework.
- strong anisotropic of both crystal and electronic structure
  layered structure – along $\bar{c}$ direction } layered Provskite type.
  perovskite within the layers.
  ⇒ 2-Dimensional s.c., except BKB.

- Cation sublattice :
  Cations are usually shifted away from idel perovskite position about 0.2 Å, and Disorder on cation sites occurs in all compounds.

⇒ Cation sublattice is deformed one. and non-stoichiometry occurs usually. This means it contains some mixed valent ions.

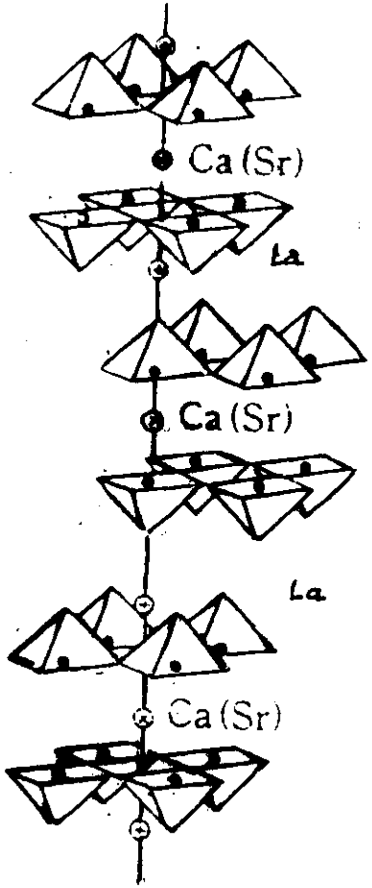


(a) Nd_2CuO_4



(b) Sr_2CuO_3

Insulator.



(c) $La_2SrCu_2O_6$, $La_2CaCu_2O_6$
×($p = 0 \sim 0.25$)
$m = 2$

(1100°C, several hours, 3K atom)

- Oxygen substructure :

The oxygen atoms fully or partially occupy the anion sites. thus leading to a considerable homogeneity range. of O_2 content.

Due to the structural complxity and defects (twins, grain boundaries), the experimentally determined oxygen content of most compounds has only an accuracy of about 5 %.

⇒ This leads to relatively poor estimates for the average formal oxidation state of Cu and Bi.

Only three types [Cu-O] polyhedra play an important role. The others don't work.

Ex. Sr_2CuO_3. — Insulator — only Cu-O chain exist in the (x,y) plane. without the mixed valence ion.

3. Related materials :

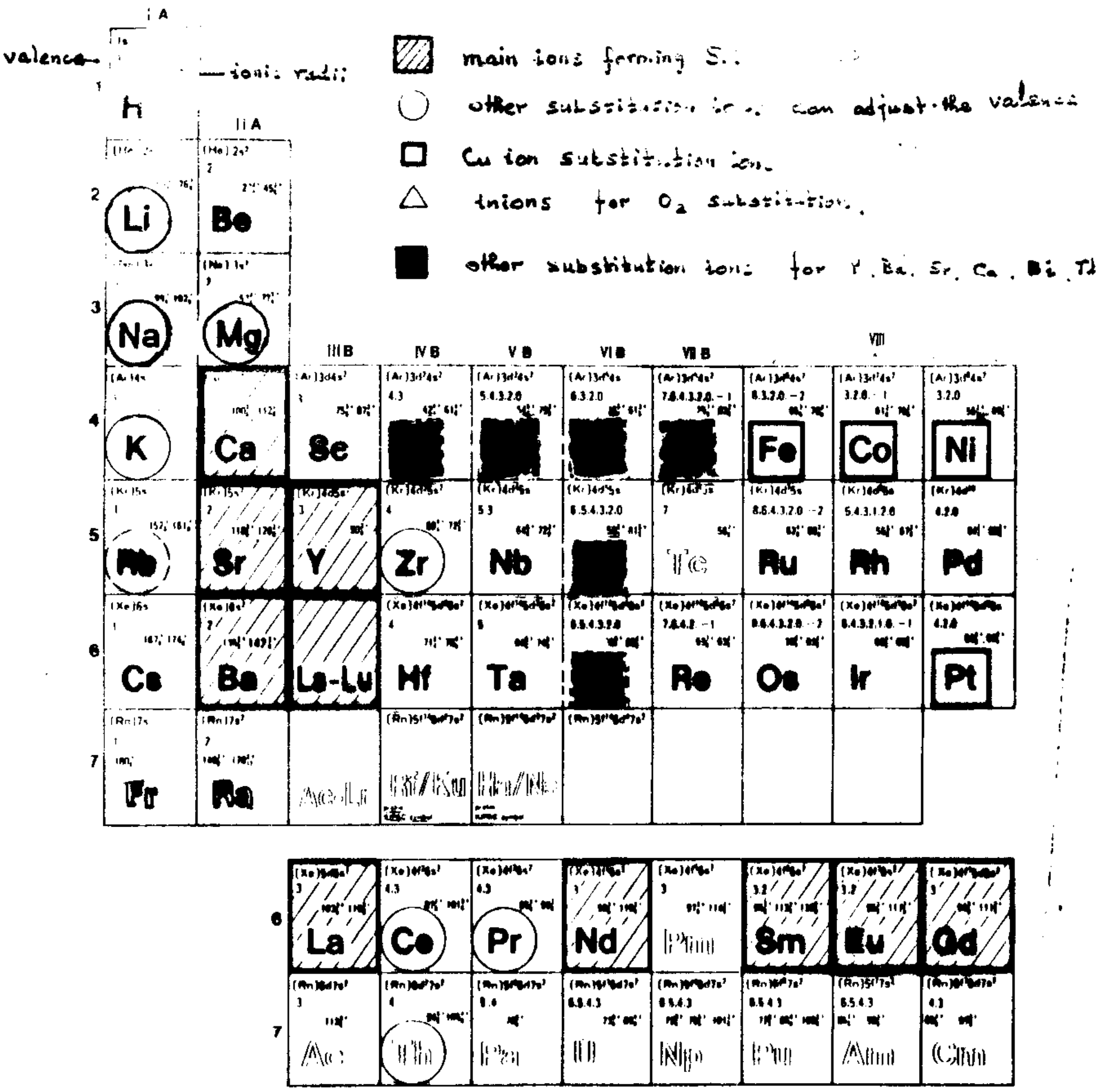
For looking for a new s.c., we have made the new compositional and structural compounds. Ex. M-doped $La_2SrCu_2O_6$ (M = Pb, Bi, C

The easy way is the substitution work.

Here, I can't list all substitution work. only show the main results in a special periodic table.

Note : It is not complet and some of their results needed to confirm.

Put your substitution work and modify the table in tim



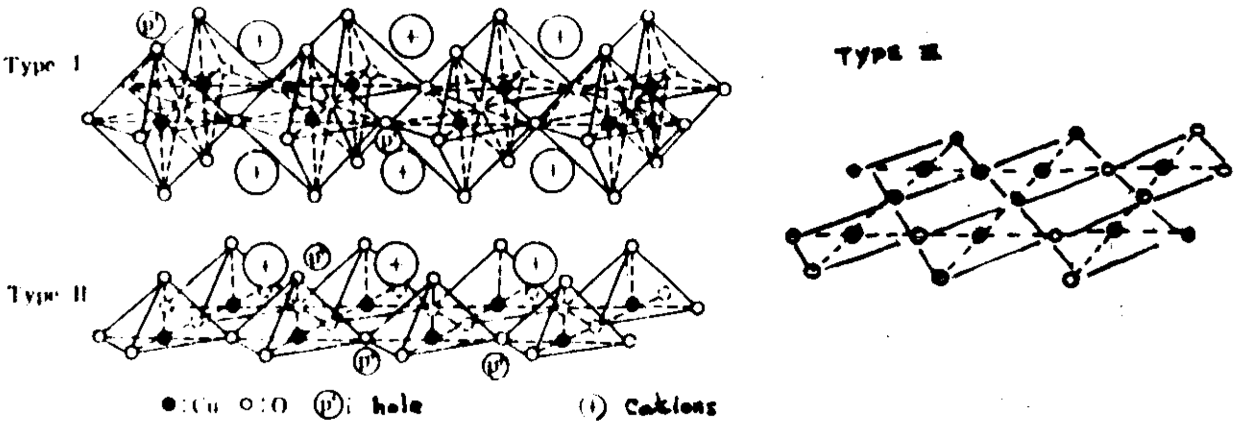
▨ main ions forming S.

○ other substitution ions can adjust the valence

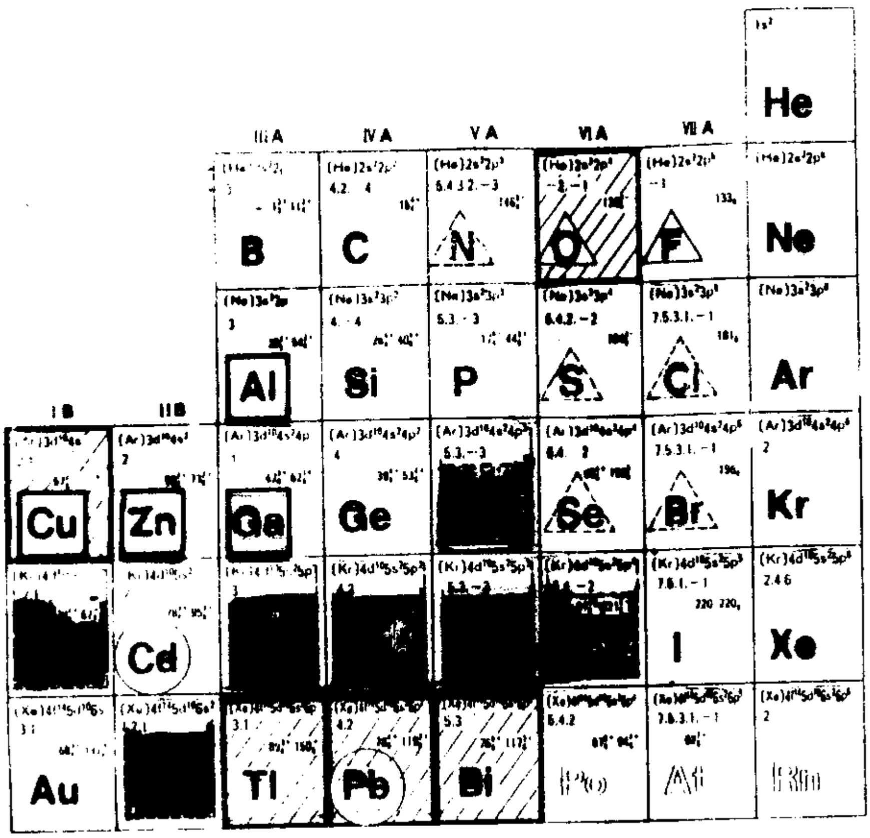
□ Cu ion substitution ions

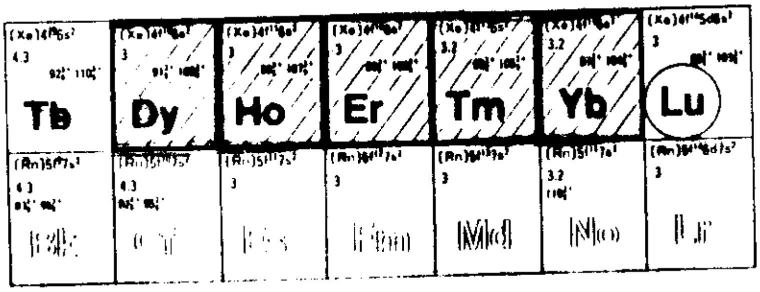
△ Anions for O_2 substitution.

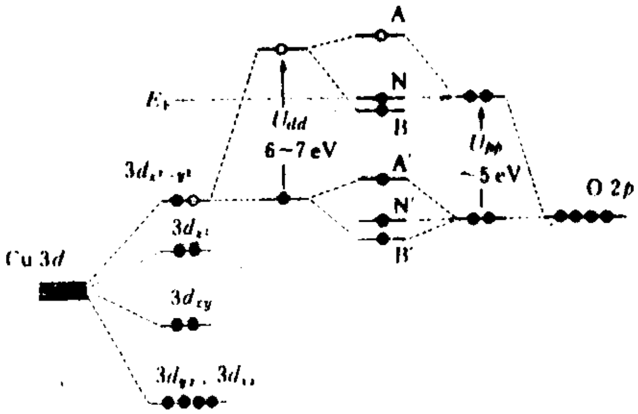
■ other substitution ions for Y, Ba, Sr, Ca, Bi, Tl



Dashed line means the possible candidate.







The second type related materials are those compounds with [Cu-O] planar. By adding the substitution ions, try to get a new one
EX: $La_2SrCu_2O_6$,

The third type ones are possible impurity phases. Here. I listed them in a table.

1. $LaCuO_{2+\delta}$, Hex , a = 3.83 Å , c = 17.10 Å
2. $BaCuO_2$, Im3m , a = 18.295 Å ;
3. $YCuO_{2.5}$, $Pna2_1$, a = 10.790 Å , b = 3.498 Å ; c = 12.452 Å
4. Y_2BaCuO_5 , Pnma , a = 12.182 Å , b = 5.658 Å ; c = 7.141 Å ;
   (Green phase)
5. Ca_2CuO_5 , Immm , a = 12.23 Å , b = 3.77 Å ; c = 3.25 Å ;
6. $CaCu_2O_3$, Pmmm , a = 9.85 Å , b = 4.11 Å ; c = 3.47 Å
7. $SrBiO_3$ Tet. a = 13.329 Å , c = 4.257 Å ;
8. $SrCuO_2$, Cmcm , a = 3.56 Å , b = 16.32 Å , c = 3.92 Å ;
9. $Bi_{2.125}Sr_{1.875}Cu_{1.03}O_y$, Pseudo-tetragonal ,
   a = 5.385 Å , c = 24.60 Å ,
10. $Bi_2Sr_3Cu_2O_y$, Or. , a = 4.888 Å , b = 5.396 Å , c = 24.804 Å ,
11. $Bi_4Sr_8Cu_5O_y$, Or. , a = 34.035 Å , b = 24.050 Å , c = 5.389 Å .

when you identify the new compound, please check the table.

(VI) New possible and Uncertain high T_c S.C :

1. $La_{2-x}Sr_xNiO_4$:

Since $La_{2-x}Sr_xCuO_4$ was discovered. Many attemps have been made to synthesize s.c with spin $s = 1$ (for Cuprates, $s = \frac{1}{2}$).

Purdue University declaimed $La_{2-x}Sr_xNiO_4$ is s.c with $T_c^{onset} = 75K$, in last year after scientists in U.S.S.R were faild to obtain s.c in the $Nd_{2-x}Ba_xNiO_4$, $Nd_{2-x}Ca_xNiO_4$, $Pr_{2-x}Ba_xNiO_4$, $Pr_{2-x}Sr_xNiO_4$ compounds.

Recently, scientists mentioned $La_{2-x}Sr_xNiO_4$ as s.c seldom, because of not reproducing in the other Lab and strange behavior of R vs T curve. Probabilly. It is not true s.c.

Doh't waste your time without the special considering.

- Preparation :

  Standard Solid state reaction does not work; Only Radio frequence induction skill melting and Bridgeman Method were used to grow single crystal.

- Low oxygen pressure annealing was required for stablizing s.c phase.

  $-7 \geq \log P_{O_2} \geq -9$. for 24h.

- Structure : Orthorhombic with S.G Bmab, it is isostructural with $La_{2-x}Sr_xCuO_4$.

- Resistance vs Temperature curve was divided into 3 parts :

  (R.T — 60K) ⟶ (60K — 40K) ⟶ below 40K

  semiconducting insulating s.c ing, $T_c^{zero} = 19K$ (?)

- Very slow cooling rate is required. for 4h from R.T to LN_2
- No Meissner effect.

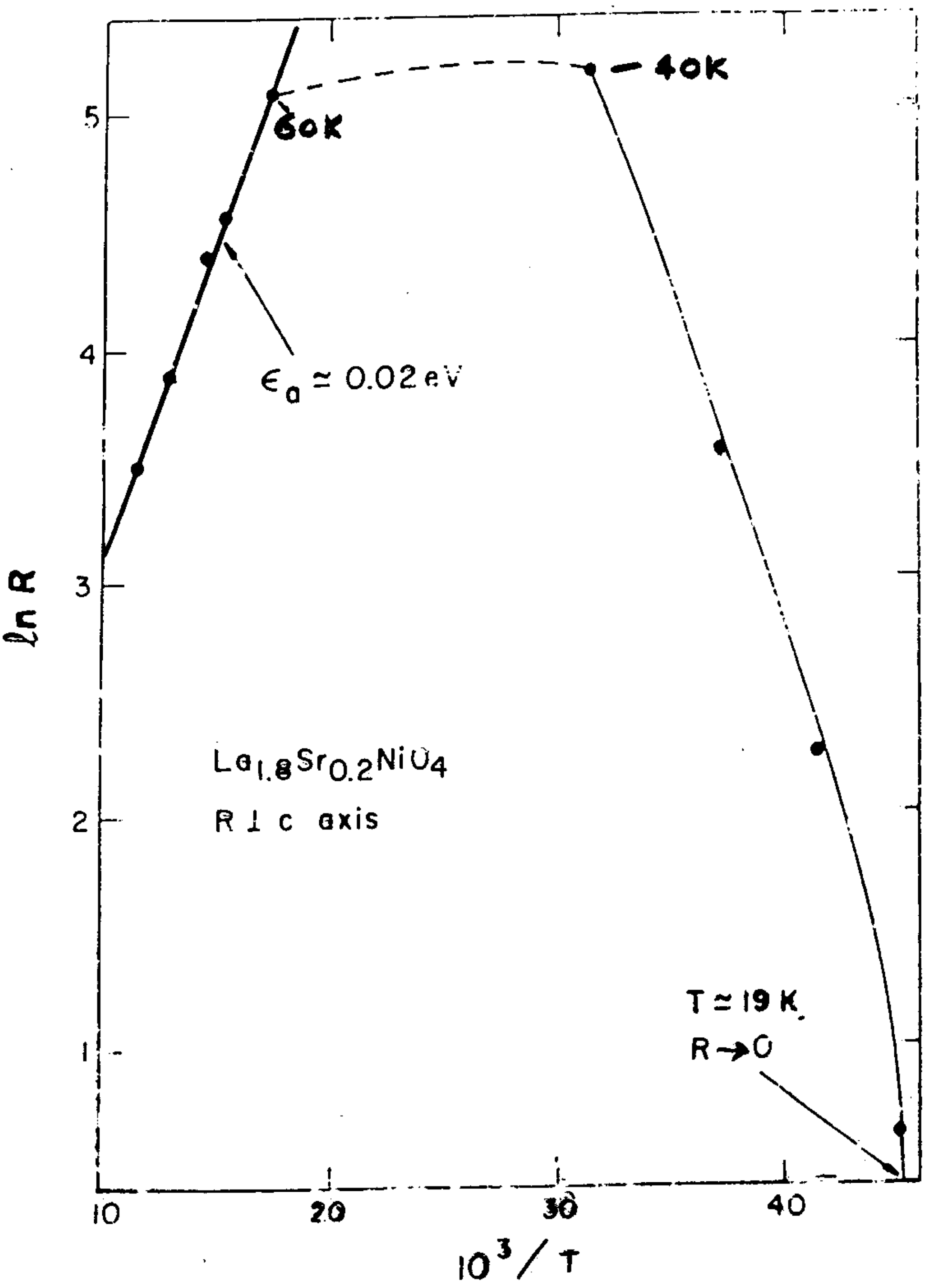


Fig 3 [illegible] J. Spalek, Z. [illegible] & [illegible] Honig

2. Sb - doped $(Bi, Pb)_2 Sr_2 Ca_2 Cu_3 O_{10+\delta}$ with $T_c = 130K$

It was reported by UCST in chine firstly.

Compound : $Bi_{1.7} Pb_{.2} Sb_{.1} Sr_2 Ca_2 Cu_3 O_x$, $T_c = 130K$

Zero - resistivity is not stable enough to observe after a couple of cycles.

No obvious Meissner effect occurs at the same temperature of T_c^{zero}.

Following their work, there were two different voice.

The first one is against Luo's work :

Ex.1, J.S. Luo , D. Michel , & J. P. chevallier, App. phys. Lett, 55 (14) 2, Oct, 1989. (France)

Only $T_c^{zero} = 109K$ was observed. and with Sb addition, a higher $T_c^{onset} = 125K$ is obtained for

$Bi_{1.7} Pb_{.2} Sb_{.1} Sr_2 Ca_2 Cu_3 O_y$, corresponding to a

multiphases.

Ex.2, India's work. (Sastry, et. al ; S. S. C, 71 No 11, 935, 1989)

$Bi_{1.7} Pb_{.2} Sb_{.1} Sr_2 Ca_2 Cu_{2.8} O_x$ samples show a sharp drop in electrical resistance between 145 and 124 K after partial melting and annealing for 50 hours.

The d.c. magnetic susceptibility shows $T_c = 109$ K.

The observed superconducting behavior is stable upon thermal cycling between 77K & 300K.

Using Sb_2O_5, not Sb_2O_3.

Ex. 3; Argonne Lab's strong voice:

$Bi_{1.8-x} Pb_{0.2} Sb_x Sr_{1.9} Ca_2 Cu_3 O_y$ in a wide range (x = 0, 0.1, 0.2, 0.3) shows no evidence of any s.c.ing transition above 110K, for single phase compounds.

Mössbauer effect measurement reveals Sb is always near +5 oxidation state..

(Dabrowski, et al; Physica C 160, 1989, (281-286))

The Second voice said the $T_c^{zero} = 132$ K was obtained in $Bi_{1.9} Sb_{0.1} Sr_2 Ca_2 Cu_3 O_y$ without Pb addition.

(Chandrahood, et al, Appl. Phys., lett., 53, (14) 2, Oct. 1989)

3. Possible S.C above 200K:

Over past three years, there have been at least ⑩ reports and publications of sharp resistance transition (some of them with T_c^{zero}) at much higher temperature (from 150K to R.T)

None is true S.C because of

1. unstable superconducting-like phenomena make it difficult to perform detailed studies for a better understanding of these phenomena and for identification of the structure and/or composition responsible for the higher T_c.

Ex. C.W. Chu's work (1987).

2. low reproducibility makes nobody can repeat the same work, except themselves by a chance.

3. No obvious Meisser effect occurs at the same temperature.

4. Other physical and chemical reasons.

5. Wrong measurement of R vs T curve.

Ex. Constant current supply satuata and cut off automatically.
fast cooling rate and temperature in not equilibrated.

*. Most promise S.C with T_c above 230K, but no Meissner effect appears at T

The mixed $Y_5Ba_6Cu_{11}O_y$ phase with transition temperature above 230K was proposed by J. T. Chen (Wayne State Univ.) in the last year.

- T_c **are found** to be thermal stable, when the samples are enclosed in an oxygen atomsphere.
- The non-linear I-V characteristics and their sensitivity to small magnetic fields near T_c resemble the behavior of a Type II S.C.

⇒ Above mentioned two reasons make some scientists thought that It is worth to do the same thing and look for the Meissner effect !

* Preparation ; standard Solid state reaction.

- Nominal composition is $Y_5Ba_6Cu_{11}O_y$.
- Y_2O_3, $BaCO_3$ and CuO powders were mixed and then calcined at 925°C for 10 h. in air.
- Regrinding and calcining powders until a dark color and a fine crystalline texture was obtained.
- The pellets, pressed under 50,000 psi, was sintered between 800°C and 950°C for 24 h. in flowing O_2, then cooled to R.T.

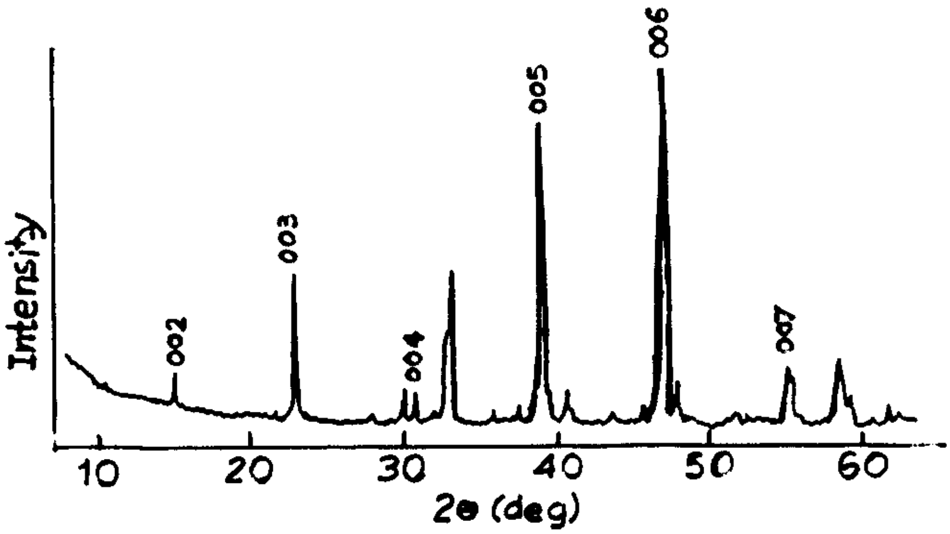
- Low temperature (70°c) oxygenation process :
  Samples in the glass desecator were slightly heated to temperature of 50°c to 70°c, by using an infrared heating lamp, for at least one week under one atomsphere of oxygen.

- All of experimental measurements were performed also in Oxygen atomasphere ($P_{O_2} = 1$ atm)

- X-ray diffraction showed the mixed phases including :
  predominate phases : $YBa_2Cu_3O_{7-\delta}$, Y_2BaCuO_5 , and CuO ;

\+ Minor unidentified phase .

- The 123 phase showed a high degree of (001) direction preference.



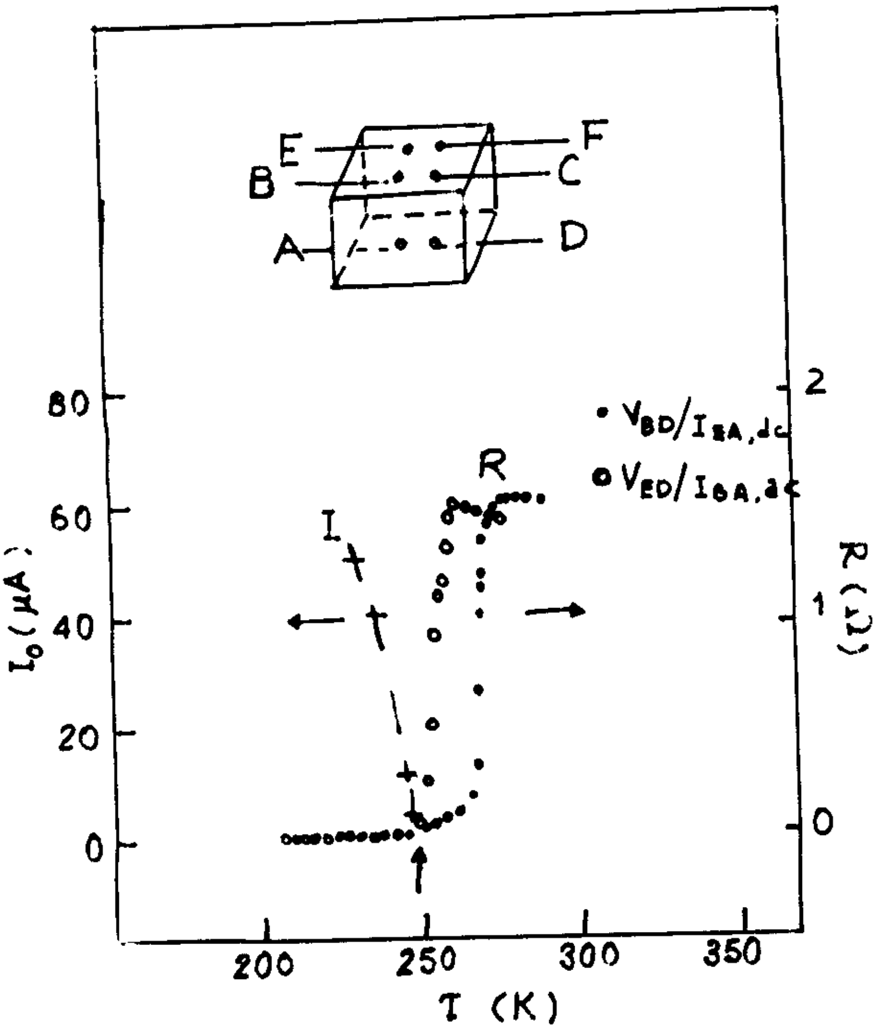
It is unclear what role the mixed phase and 001 preference play in leading to the formation of 230k phase. But, both are necessary for the observation of 230K.

* Results :

- T_c occurs in the temperature range of 235 K to 250 K for different thermal cycles and various electrical path way.

⇒ T_c^{zero} is stable enough to observe in O_2 cuviroment.

- No Meissner effect occurs at the same T_c.



- Hard reproduce

a lot of trick !

Waiting for χ !