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**EXPERIMENTAL WORKSHOP ON
HIGH TEMPERATURE SUPERCONDUCTORS
(11 - 22 April 1988)**

THE CRYSTAL CHEMISTRY & STRUCTURES OF HIGH T_c SUPERCONDUCTING OXIDES

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These are preliminary lecture notes, intended only for distribution to participants.

The crystal chemistry & structures of high Tc superconducting oxides

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What is the high Tc superconductor ?

discovery of 35K $La_{2-x}Ba_xCuO_{4-y}$
(Bendnotz & Müller)

finding of 90K $YBa_2Cu_3O_{7-x}$
(Chu , Zhao, Tarnaka)

finding of 85 – 110K Bi-Sr-Ca-Cu-O oxides
(maeda) based on Bi-Sr-Cu-O oxide
(Michel & Raveau)

finding of 100 – 125K Tl-Ba-Ca-Cu-O oxides
(Hermman & sheng)

All of high Tc superconductors :
layer distorted - perovskite structure
or layer Bismuth structure
< Bi_2O_2 double layers + distorted perovskite.

what is the perovskite structure ! (fig 1)

stabilization of cubic perovskite :
radii of A and B cations satisfy

$$R_A + R_O = t * 2 (R_B + R_O)$$

$$.8 \leq t \leq .9$$

$$R_A > R_B$$

For the distorted perovskite, t takes large range of value.

Basic informations : Cubic , Pm3m
$a \doteq 3.9$ Å

Second represent of perovskite structure.
(see fig.2)

The features of ideal perovskite :

a. Not contain close packed oxygen ions

b. B–O chain → B – O sheet → B–O 3 dimensional framwork.

Ideal $AB O_3$ type perovskite:

examples: $CaTiO_3$, $SrTiO_3$ (fig. 1)

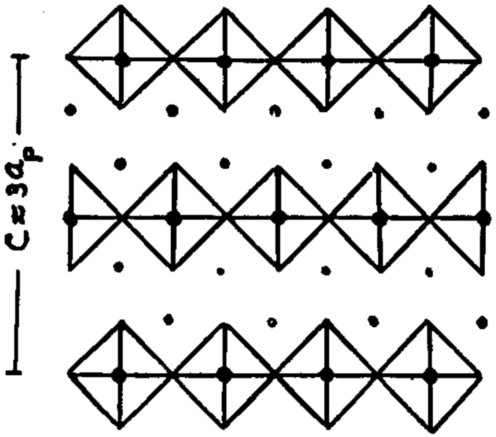
distorted order:

Cubic → Tetragonal → Orthorhombic

high temperature   low temp. phase

. Perovskite-related structure

K_2NiF_4 type : La_2CuO_4 & $La_{2-x}Sr_xCuO_4$

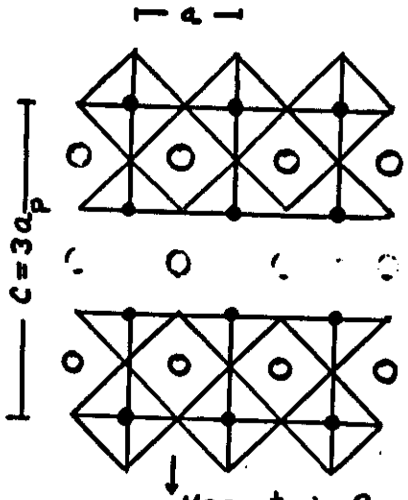


ABO_3 type & derivation

$ABO_3 \longrightarrow A_mB_mO_{3m-1}$ (m = 2, 3, 4, 5)

m = 3

A = Y and Ba , B = Cu



$YBa_2Cu_3O_9 \longrightarrow YBa_2Cu_3O_8 \rightarrow YBa_2Cu_3O_{7-\delta}$

How to determine the structure:

techniques:
. x-ray powder diffraction (profile refinement) — Rietveld Method
.. x-ray single crystal diffraction (four circles diffractometer)
... neutron powder scattering - Rietveld
:: electron microscopy.

Superconducting phase in Y-Ba-Cu-O syste

a. phase relations in YBCO system & stable phases: $YBa_2Cu_3O_{7-x}$

b. $T_c \geq 90K$, A.c. χ or Meissner effect

anisotropic resistance measurement:

c direction : m → semi → SP

a-b plane : m → SP

c. Symmetry & space Group: Orthorhombic . Pmmm ④

d. phase transition : Tr. $\xrightarrow{750°C}$ Or.

Lattice constants change anisotropiclly with the T_q and Oxygen content,

a↑, b↓, C↑ (V↑) when O change from 7.0 to 6.5 (O

a=b, c↑ when O from 6.5 to 6.0.

Two plateaus: 90K (7.0 – 6.75); 60K (6.75 – 6.45)

e. DTA, TG: No thermal effect $\xrightarrow{at\ 750°c}$ low enthalpy

weight loss on heating (max. at 500°c)

weight gain on cooling in air

f. Structure of 1-2-3 compound (Or)

1. triple layers perovskite
2. one dimensional Cu-O chain in $\vec{b}$ axies
3. Basic data: (see table)

g. microstructure: inhomogeneous compositic

Twin; domain, stacking fault,

Amorphous.

h. Structure of Non-superconducting $YBa_2Cu_3O_6$

tetragonal . S.G. P4/mmm ⑥

{ oxygen amount : 6.5 ≥ x ≥ 6.0
{ distribution of oxygen: Vacant in b axies.

→ No Cu – O – Cu – O chain

No twin, No domain

composition influctuation

Semiconductivity. until 4.2K

Commen structure features of $YBa_2Cu_3O_7$ & $YBa_2Cu_3O_6$

triple layers < 3 subcell of Perovskite; Ba - Y - Ba - Ba - Y ordering along $\vec{c}$

Cu – O bond length ~ 1.95Å

Uncertain things about 1-2-3:

1. Oxidation state or valence of Cu ion
   Cu^{+}, Cu^{++}, Cu^{+++} or Cu^{++}/Cu^{+++} mixture
   2.3 ? XADES, XPS, ESR.
2. dimensionality: 1, 2, or 3?
3. exact role of oxygen ?
4. role of defects ?
   Low critical current density
   10^3 amps/cm² (bulk sample) → 10^4 A/cm²
5. isotopic effect: $O^{18} \to O^{16}$. $Cu^{31} \to Cu^{29}$

⑦

for $La_{2-x}Sr_xCuO_{4-y}$ $\Delta T \sim 0.5$ K
$YBa_2Cu_3O_{7-x}$ $\Delta T \sim 0.3$ K
O^{18}

for $YBa_2Cu_3O_{7-x}$
no obvious isotopic effect for Cu
no support BCS. No against BCS.

6. C parameter jump when O = 6.5
Very small jump of c parameter due to the Bond length of Cu-O bond along C axies
Is it the true reason for 90K superconductivity?

7. Patial ordering of oxygen vacances along $\bar{b}$ axies,
It is not confirmed by others.

⑧

Superconducting phases in La-Ba-Cu-O system

ABO_3 type $LaBa_2Cu_3O_{7-x}$ (80K)
K_2NiF_4 type $La_{2-x}Ba_xCuO_{4-y}$ (30-40K)

$LaBa_2Cu_3O_{7-x}$ — $LaBaCu_2O_{5-x}$ (or $La_3Ba_3Cu_6O_{15-x}$)
Solid solution
structure change contineously.
Tc from 80K to 40K be adjusted
→ La & Ba ordering not necessary

$La_{2-x}Ba_xCuO_{4-y}$:

La_2CuO_4 stoichiometric compound
— semiconductivity until 4.2 K
$La_2Cu_{1-x}O_{4-y}$ non stoichiometric
— superconduativity at 30~40K
only can synthesize at high temperature and high oxygen pressure.

La_2CuO_4 by adding Ba
Orthorhombic → tetragonal

Cu-O chain ?

Substitution of Y

most of rare earths except of Ce, Pr, Pm, T
the other 3+, 4+ elements

F-O compound; 150K ? X

Substitution of Ba, (mono, di-, tri-valence)

Cu is absolutely necessary.

Four critiria for serching of new or high T_c superconductors:

- . Zero resistivity
- .. Meissner effect
- ... high stability
- :: high reproducibility

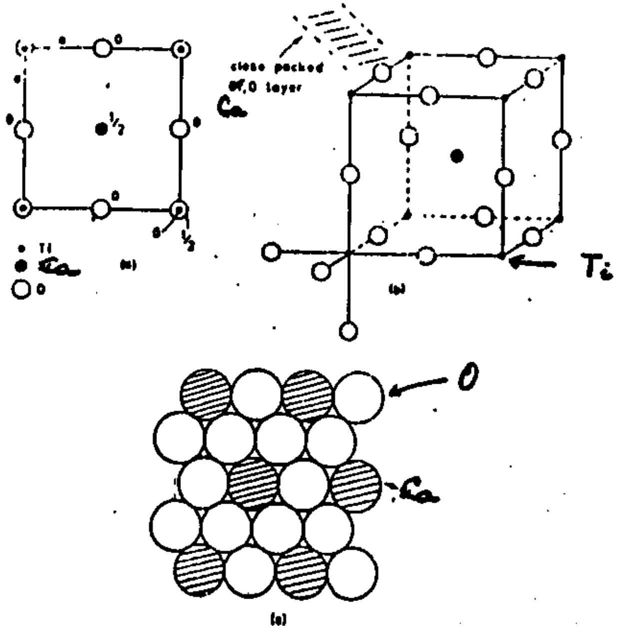
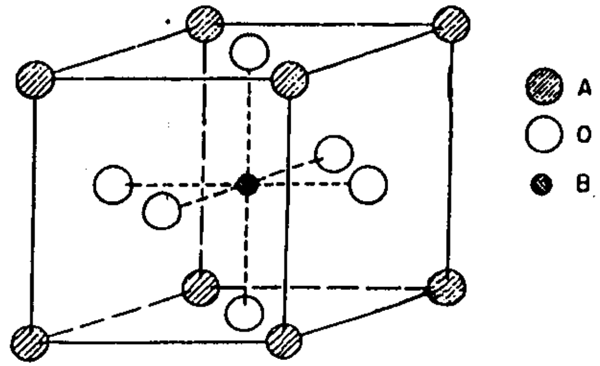


Fig 1



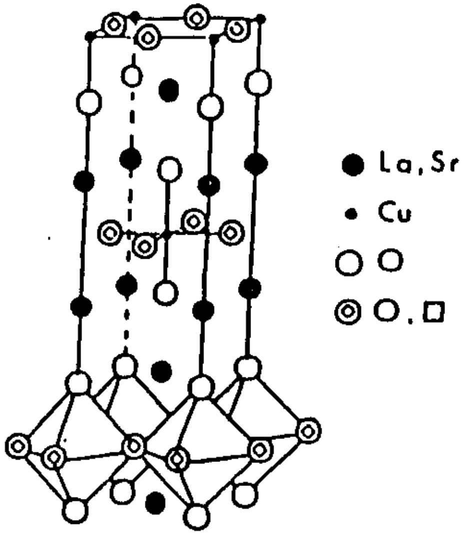
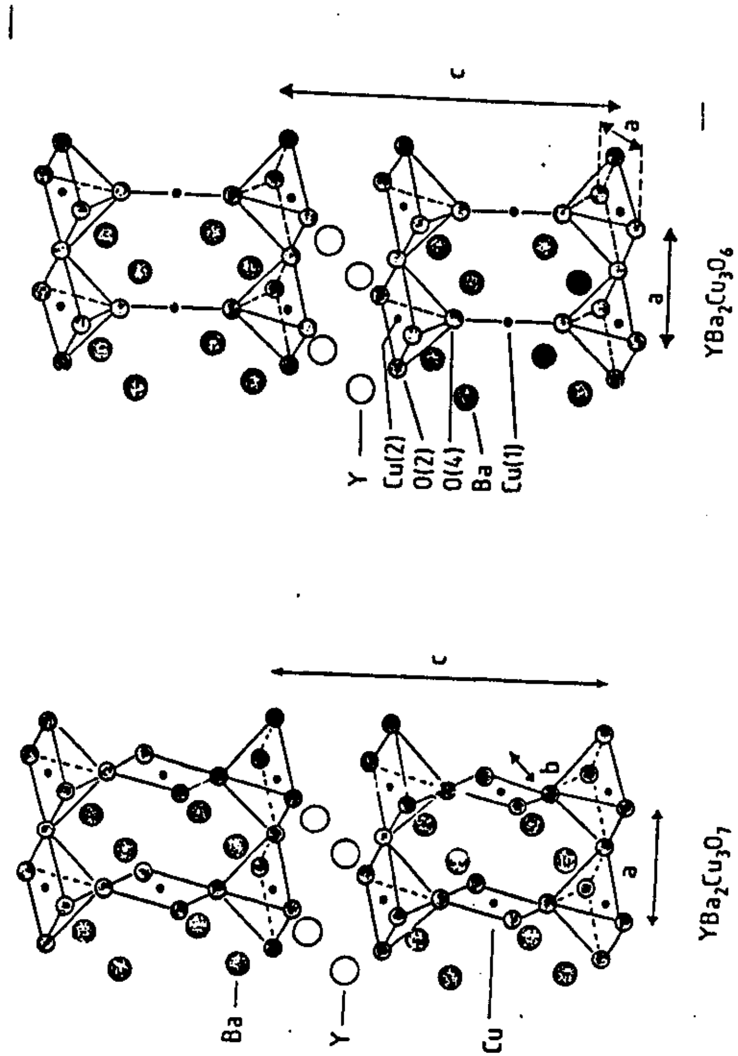
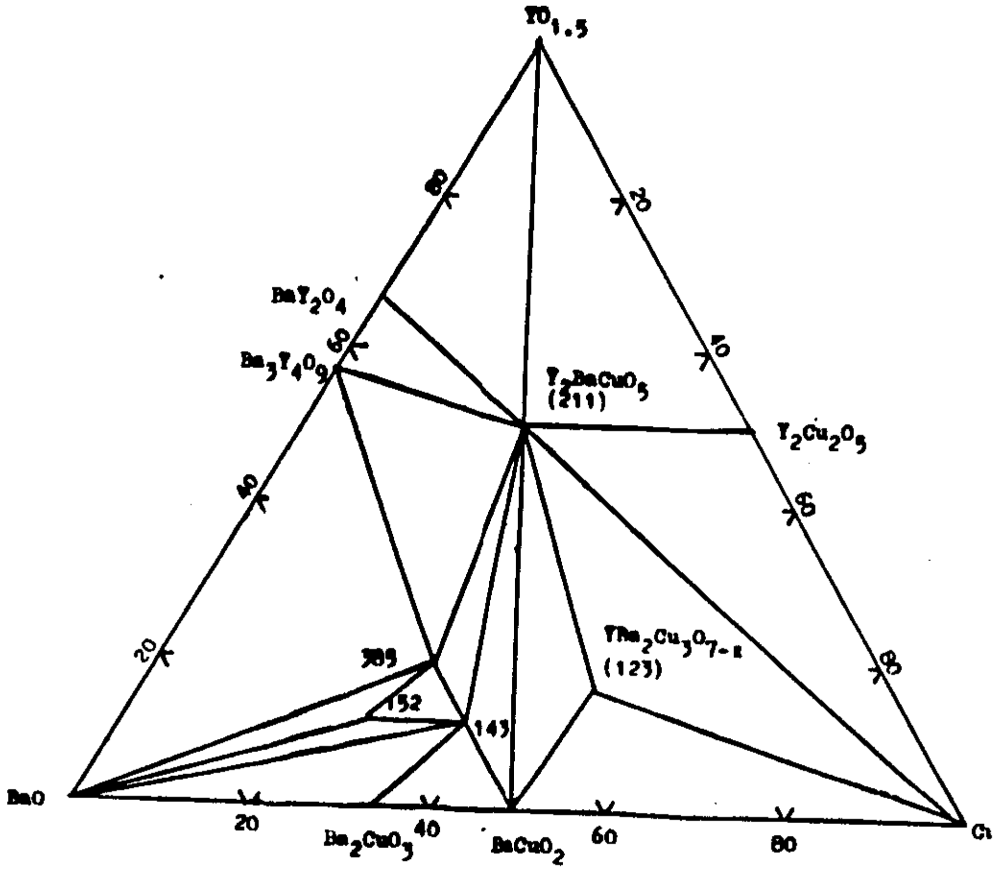


Fig 3 a)



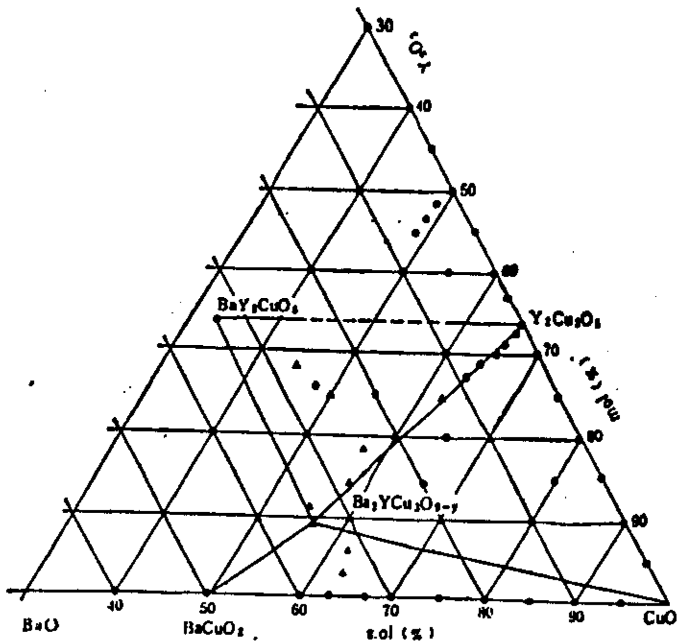


Ainks & philips Lab.

The stable phases in Y_2O_3 - BaO - CuO system

Compound	Symmetry	Lattice constants (Å)
$BaCuO_2$	Cubic	a = 18.26
Ba_2CuO_3*	?	
$Ba_2Y_2O_5$	Tetragonal	a = 3.3771, c = 11.852
BaY_2O_4	Orthorhombic	a = 10.388, b = 12.00, c = 3.448
$Y_2Cu_2O_5$ (green)	Orthorhombic	?
Y_2BaCuO_5 (211) (green)	Orthorhombic	a = 7.123, b = 12.163, c = 5.669
$YBa_2Cu_3O_{7-x}$ (123) (black)	Orthorhombic, superconducting phase	a = [illegible], b = 3.889, c = 11.6[illegible]
$YBa_2Cu_3O_6$ (high Temp.) phase	Tetragonal	a = 3.8648, c = 11.763
$YBa_4Cu_3O_{8.5}$	?	
$YBa_5Cu_2O_{8.5}$	?	
$Y_3Ba_8Cu_5O_{17.5}$	?	

\+ Y_2O_3
CuO
BaO



(F. Institute of physics. Beijing)

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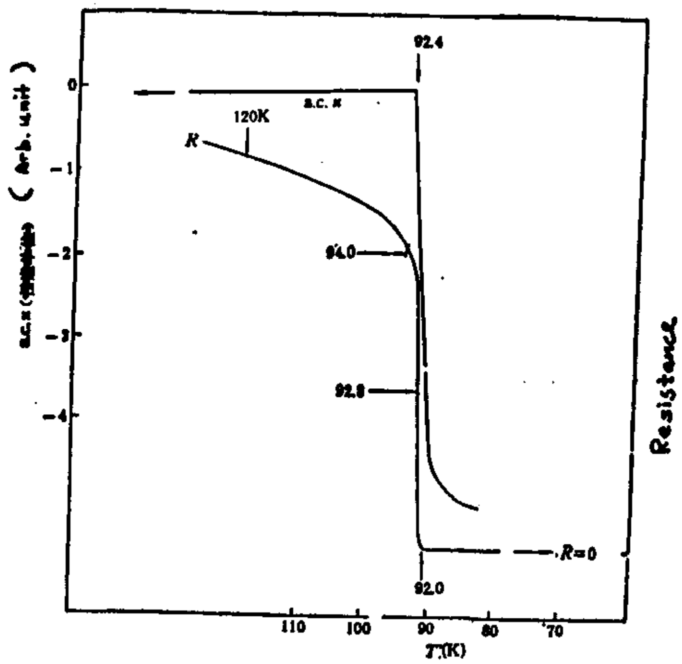

Fig 5.

R vs T & A.C. χ vs T
for the bulk sample.

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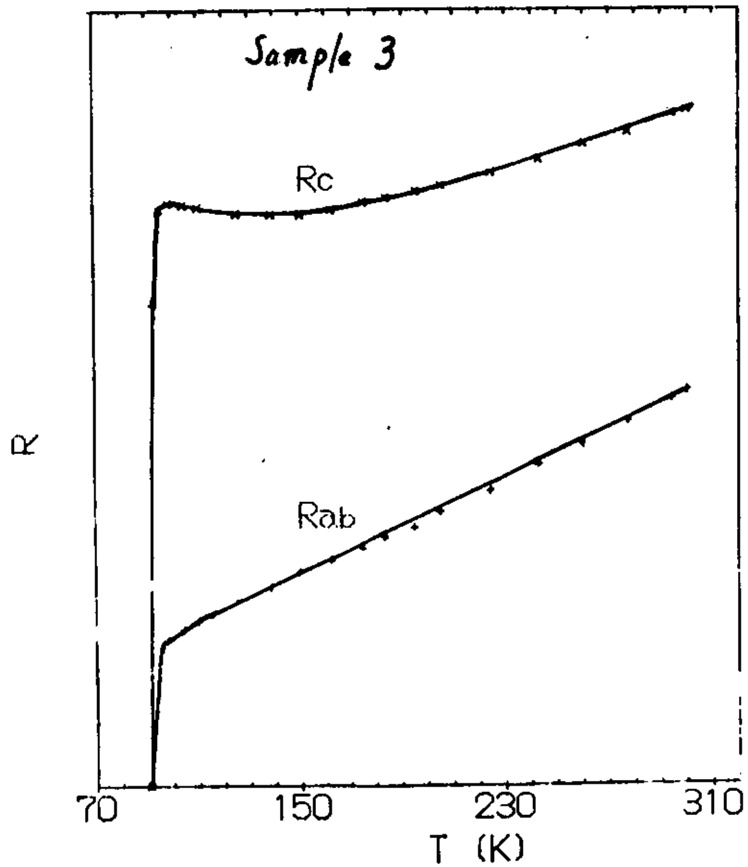
anisotropic resistivity vs temperature curves of the small single crystal.



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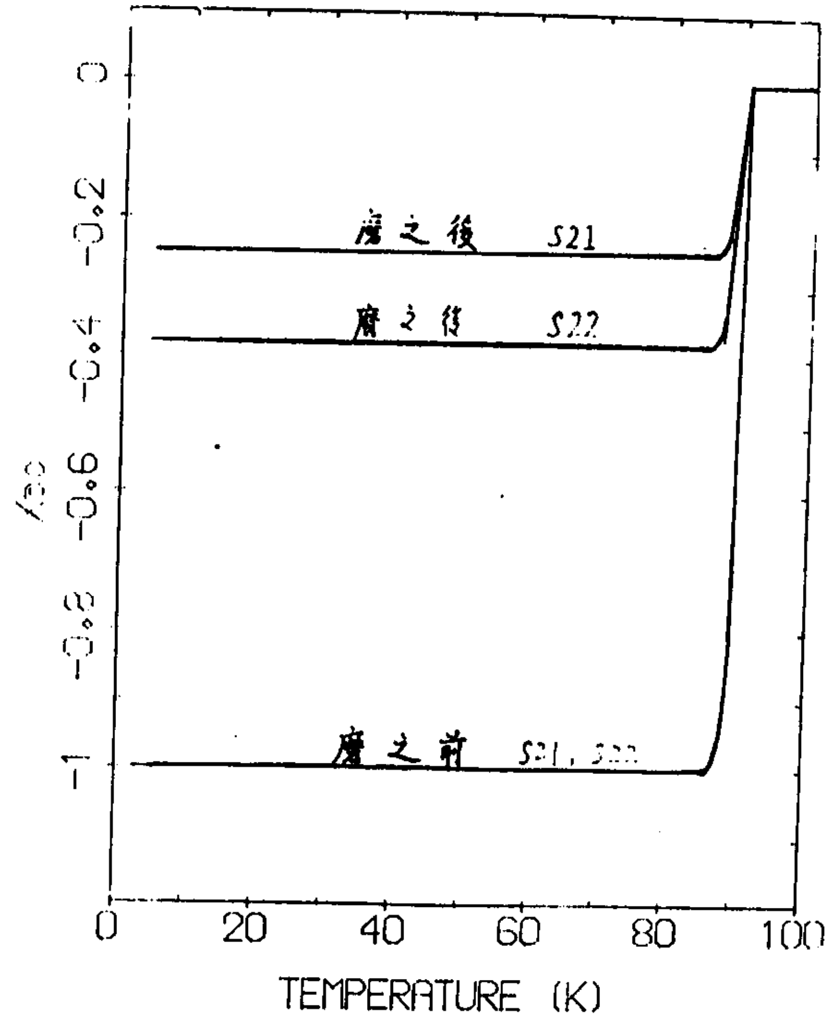

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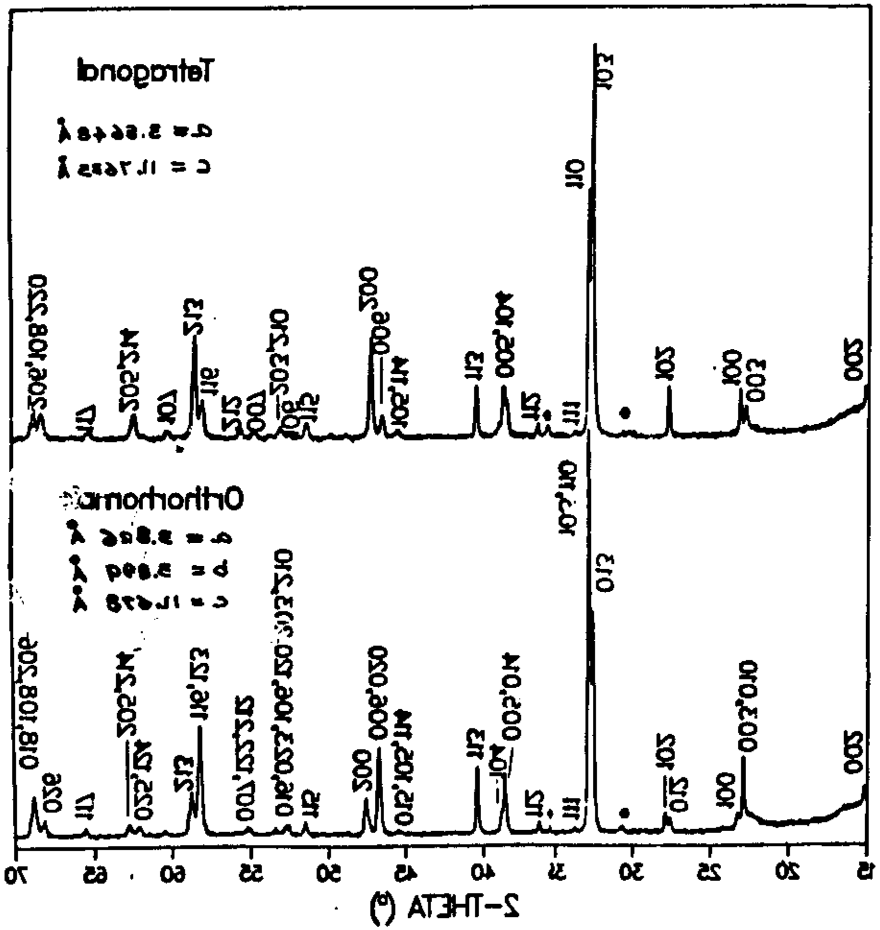

After A. M. Kini, Argo

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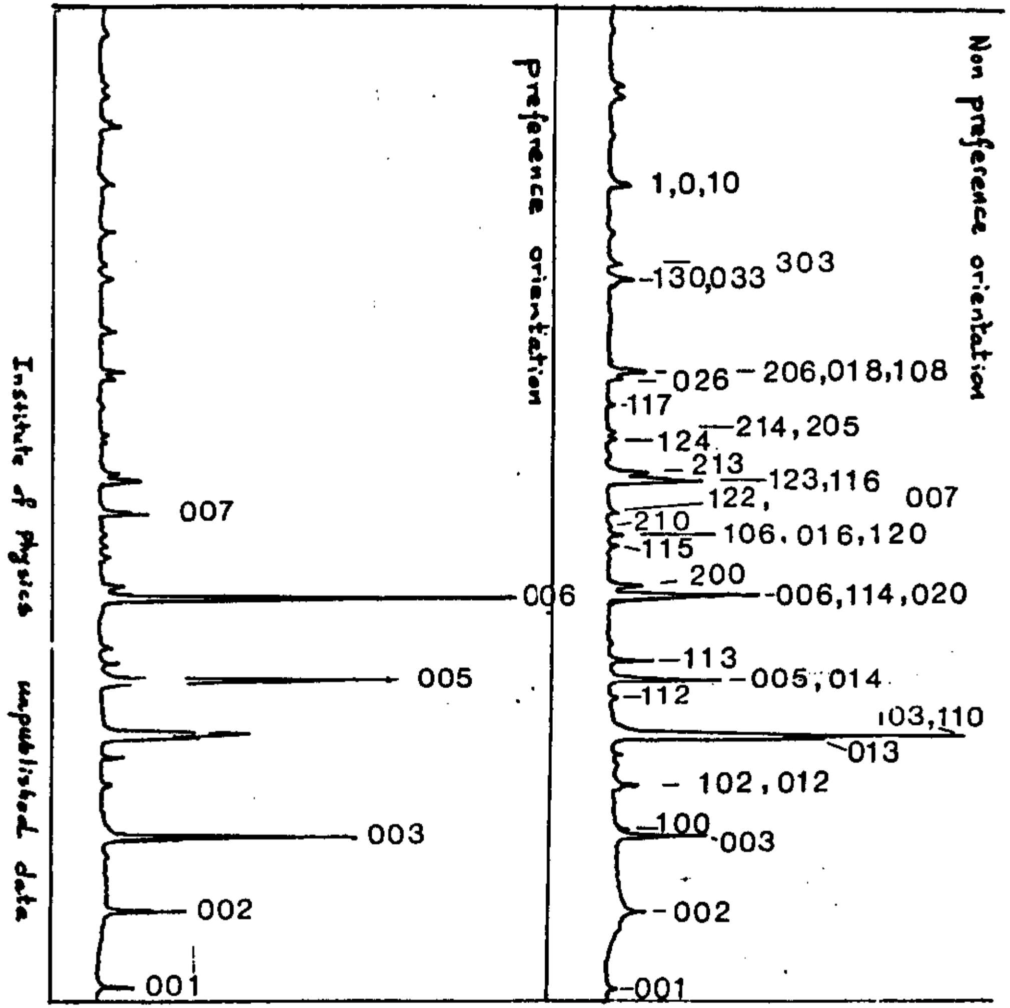

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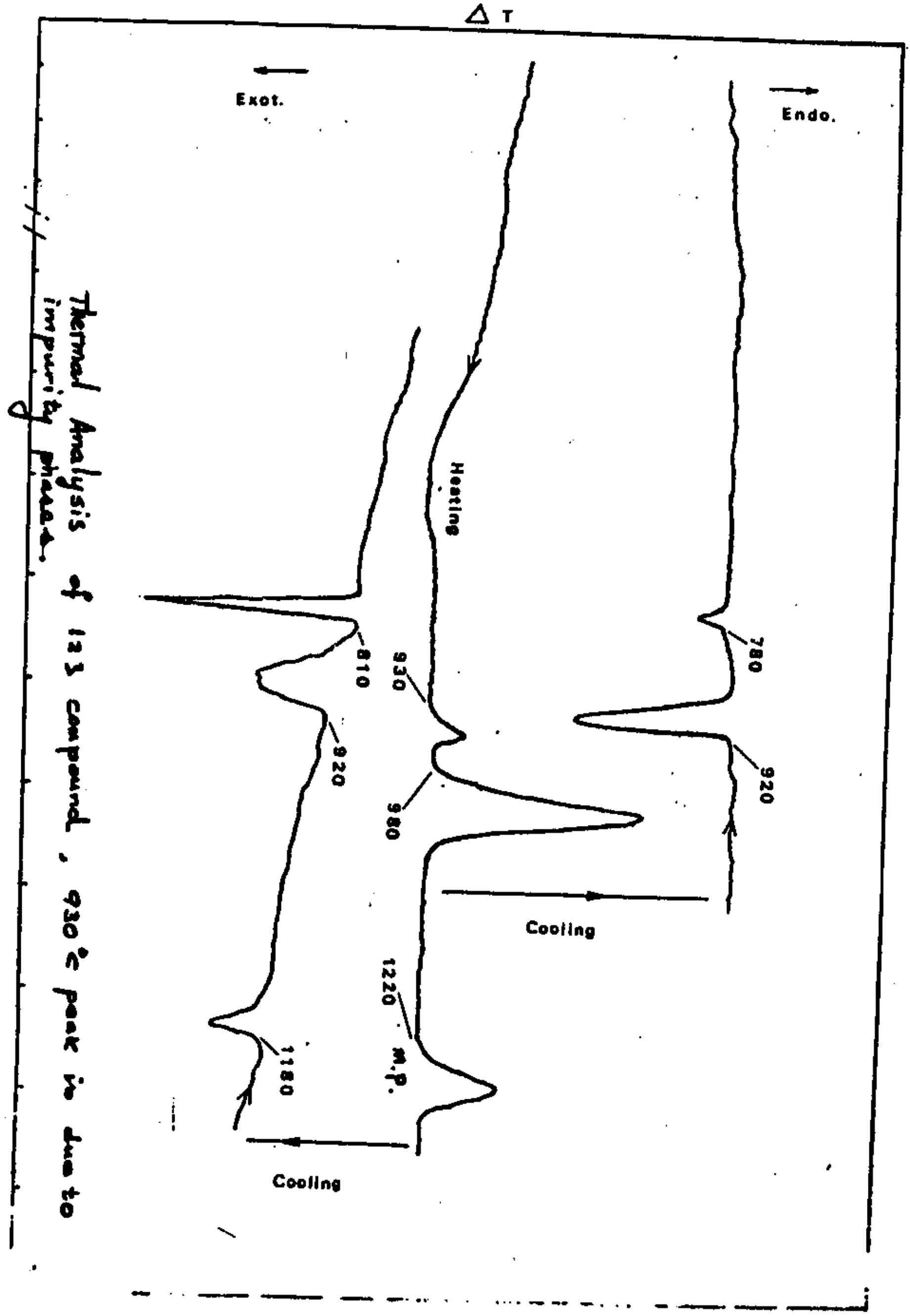
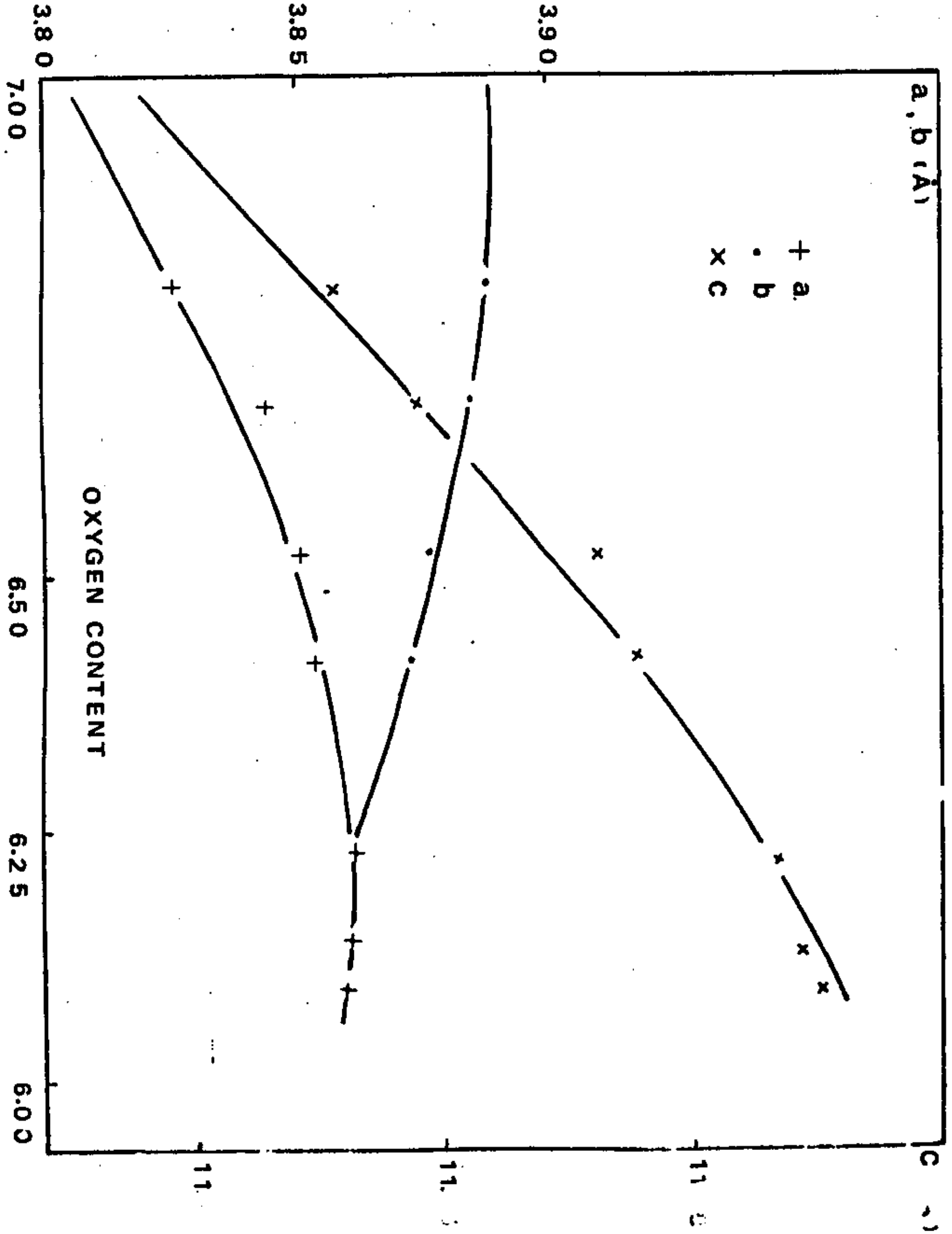
fig 4. d

$YBa_2Cu_3O_{7-x}$ x-ray data

h	k	l	d_{OBS} (Å)	I/Io (%)
0	0	1	~ 11.76	< 2
0	0	2	5.844	2
0	0	3	3.893	11
1	0	0	3.822	3
0	1	2	3.235	3
1	0	2	3.198	5
0	1	3	2.750	60
1	0	3	2.726	100
1	1	0		
1	1	1	2.653	2
1	1	2	2.469	3
[illegible]	0	5	2.336	11
1	0	4	2.321	3
1	1	3	2.232	13
0	2	[illegible]	1.946	23
0	0	6		
2	0	0	1.911	'0
1	1	5	1.775	3
0	1	6	1.741	2
0	2	3		
1	0	6	1.734	2
1	2	0		
2	0	3		
2	1	0	1.716	2
1	2	1		
1	2	2	1.662	1



Thermal Analysis of 123 compound, 930°C peak is due to impurity phase.



After Marion et al

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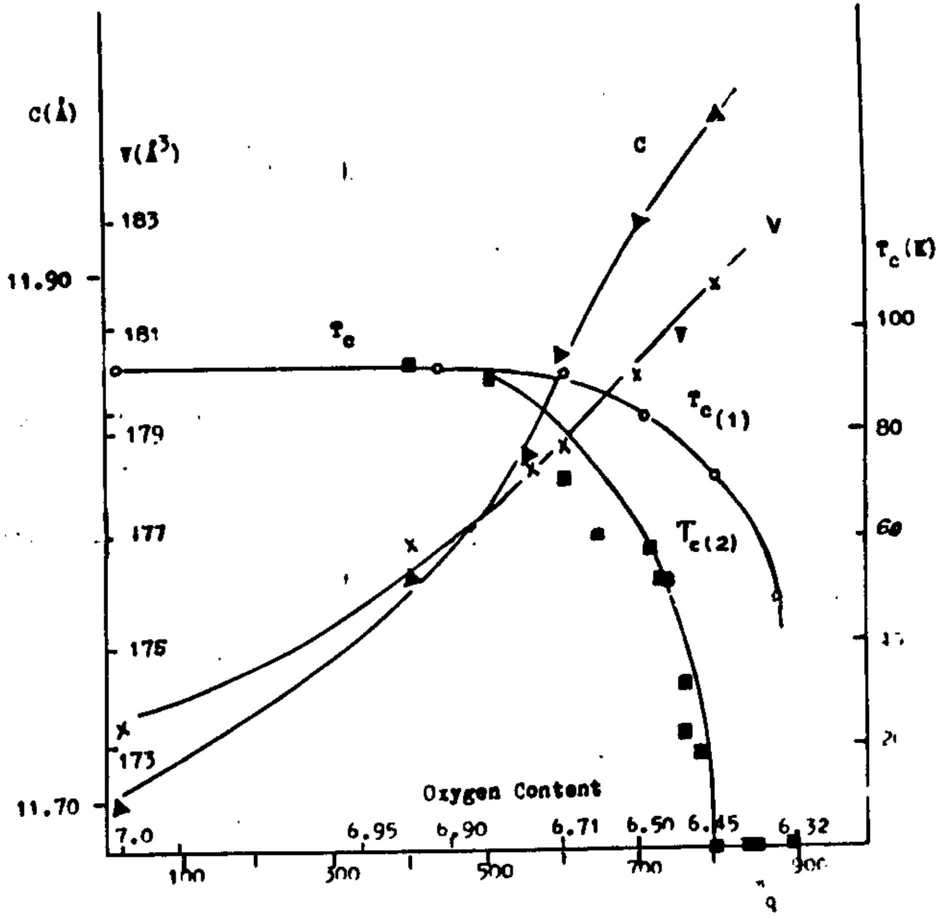

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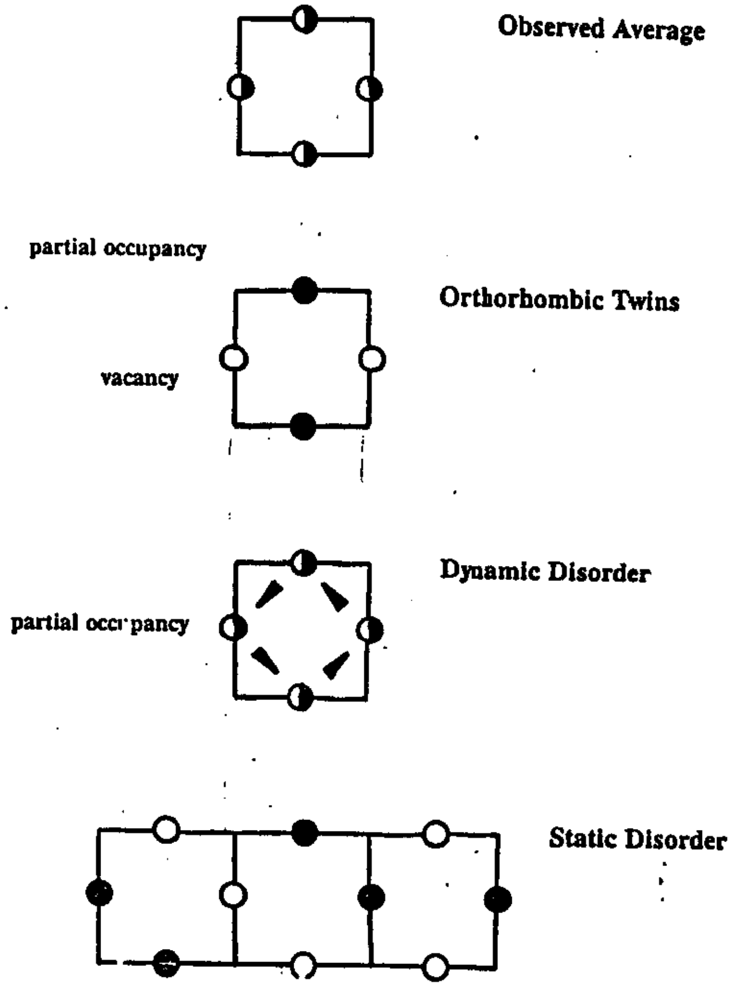

The models for twin

Table II: Atomic parameters

Atom	Parameter	$YBa_2Cu_3O_6$ (this work) a=3.865(1) Å c=11.852(3)Å P4/mmm	$YBa_2Cu_3O_6$ (Santoro et al.) (4) a=3.8570(1)Å c=11.8194(3)Å P4/mmm	$YBa_2Cu_3O_7$ (Beno et al.) (13) a=3.8231(1)Å b=3.8863(1)Å c=11.6809(2)Å Pmmm	$YBa_2Cu_3O_7$ (Capponi et al.)(14 a=3.8206(1)Å b=3.8851(1)Å c=11.6757(4)Å Pmmm
Y	x	.5	.5	.5	.5
	y	.5	.5	.5	.5
	z	.5	.5	.5	.5
	u_{11}	.0053(2)			
	u_{22}	.0053(2)	u_{iso}=.0092(5)	u_{iso}=.0058(5)	u_{iso}=.0073(14)
	u_{33}	.0086(3)			
	occ.	1	1	1	1
Ba	x	.5	.5	.5	.5
	y	.5	.5	.5	.5
	z	.1951(2)	.1952(2)	.1843(3)	.1841(4)
	u_{11}	.0085(1)			
	u_{22}	.0085(1)	u_{iso}=.0063(5)	u_{iso}=.0068(6)	u_{iso}=.0075(14)
	u_{33}	.0100(1)			
	occ.	1	1	1	1
Cu(1)	x	0	0	0	0
	y	0	0	0	0
	z	0	0	0	0
	u_{11}	.0139(4)			
	u_{22}	.0139(4)	u_{iso}=.0127(5)	u_{iso}=.0063(6)	u_{iso}=.0048(14)
	u_{33}	.0113(5)			
	occ.	1	1	1	1
Cu(2)	x	0	0	0	0
	y	0	0	0	0
	z	.3609(1)	.3607(1)	.3556(1)	.3549(3)
	u_{11}	.0043(2)			
	u_{22}	.0043(2)	u_{iso}=.0062(4)	u_{iso}=.0037(5)	u_{iso}=.0065(9)
	u_{33}	.0122(4)			
	occ.	1	1	1	1

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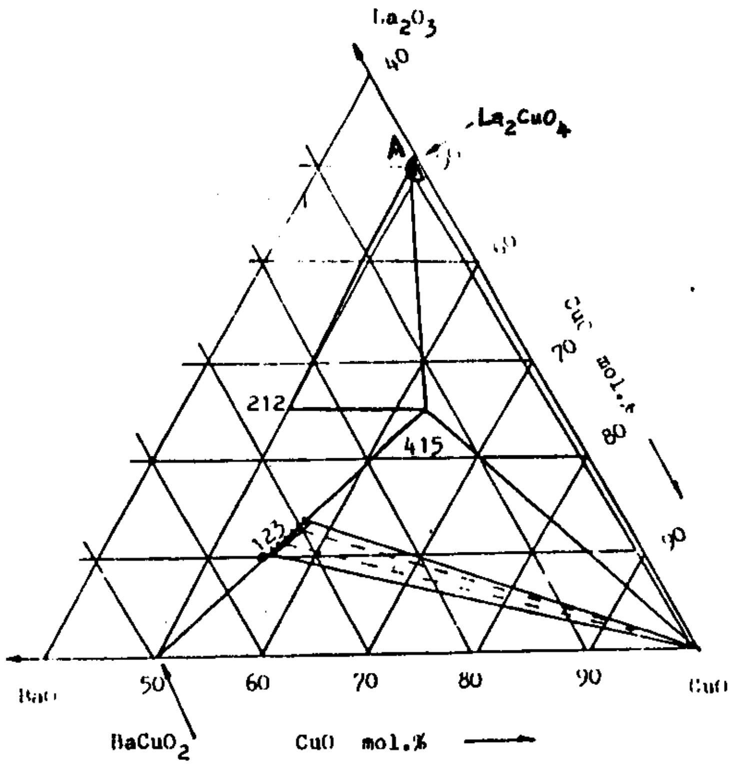

Fig. 2 The phase diagram of La-Ba-Cu-O system in CuO-rich region. 212 and 415 refer to the non-superconducting phase compositions $La_2BaCu_2O_6$ and $La_4BaCu_5O_{14.7}$, respectively. The phase at place A is $La_{2-x}Ba_xCuO_4$ ($0 \leq x \leq 0.07$). The hatched line indicates the region of solid solution which has an ideal composition $LaBa_2Cu_3O_y$.

After Che et al. and Dong et. al. (Inst. of Phys)

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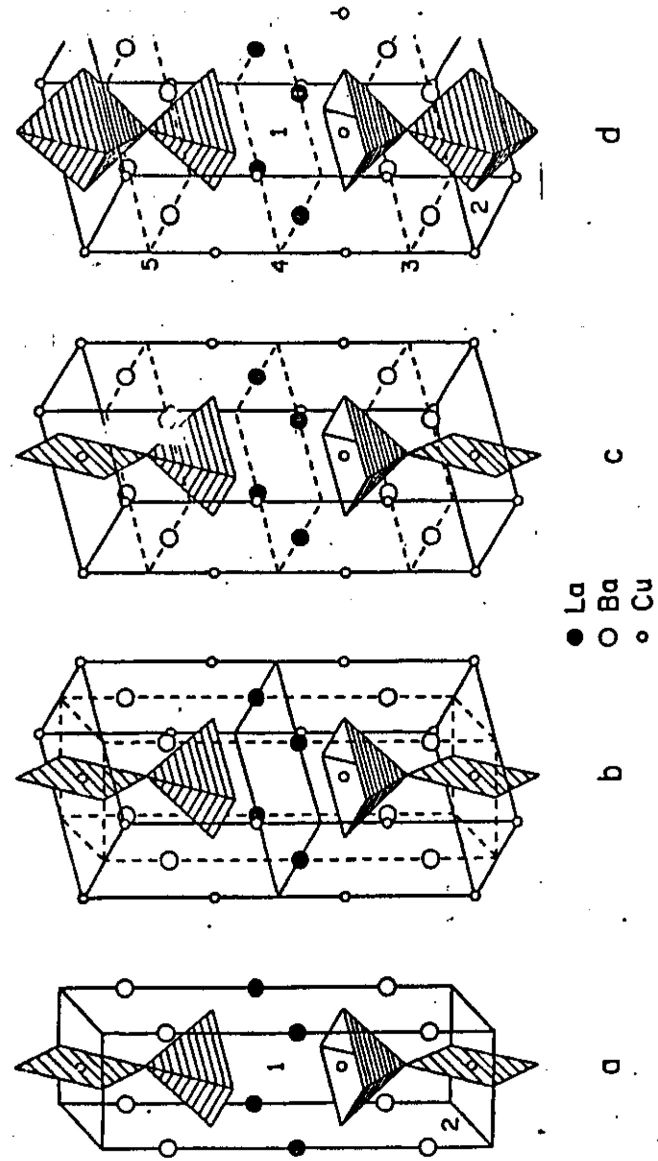

(a) 123 compound, (b) $a=\sqrt{2}\,a_p$

(28)