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SMR/543 - 9

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

(11 February - 1 March 1991)

" Structural Effects in $YBa_2Cu_3O_7$ "

presented by:

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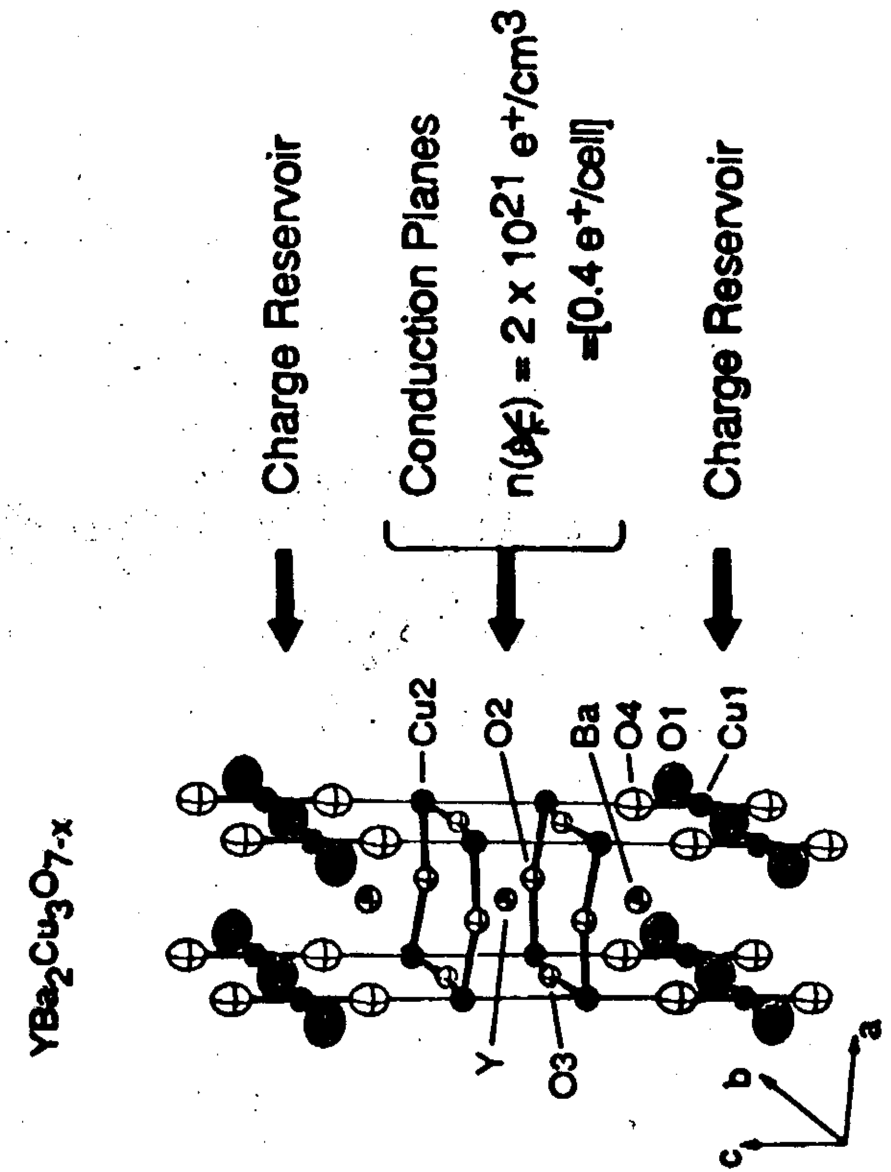
Structural Effects in $YBa_2Cu_3O_7$

Outline

- Neutron Diffraction
- The $YBa_2Cu_3O_7$ Structure
- Oxygen Ordering in $YBa_2Cu_3O_7$
  - Experimental Results
  - Theoretical Model
- Neutron Diffraction Study of $ErBa_2Cu_3O_{6+\delta}$
- Substitution of Y in $YBa_2Cu_3O_7$
- Substitution of Ba in $YBa_2Cu_3O_7$
  - Neutron Diffraction Study of $Nd(Ba_{2-x}Nd_x)Cu_3O_{7+\delta}$
- Double Substitutions
  - Role of Ionic Radius



Neutron Diffraction

Advantages :

can "see" oxygen
can "see" magnetic moments easily

Disadvantages :

needs large samples
not available in ordinary laboratory
has large average sampling volume

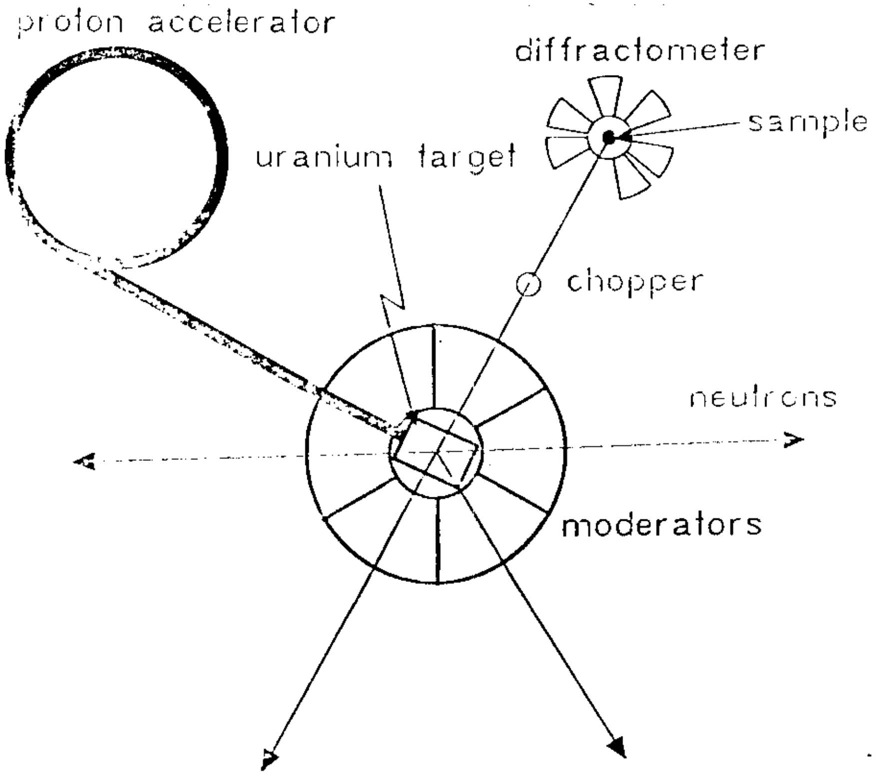
Neutron generation :

reactor → monochromator → θ-2θ scan
spallation → moderator → T.O.F.

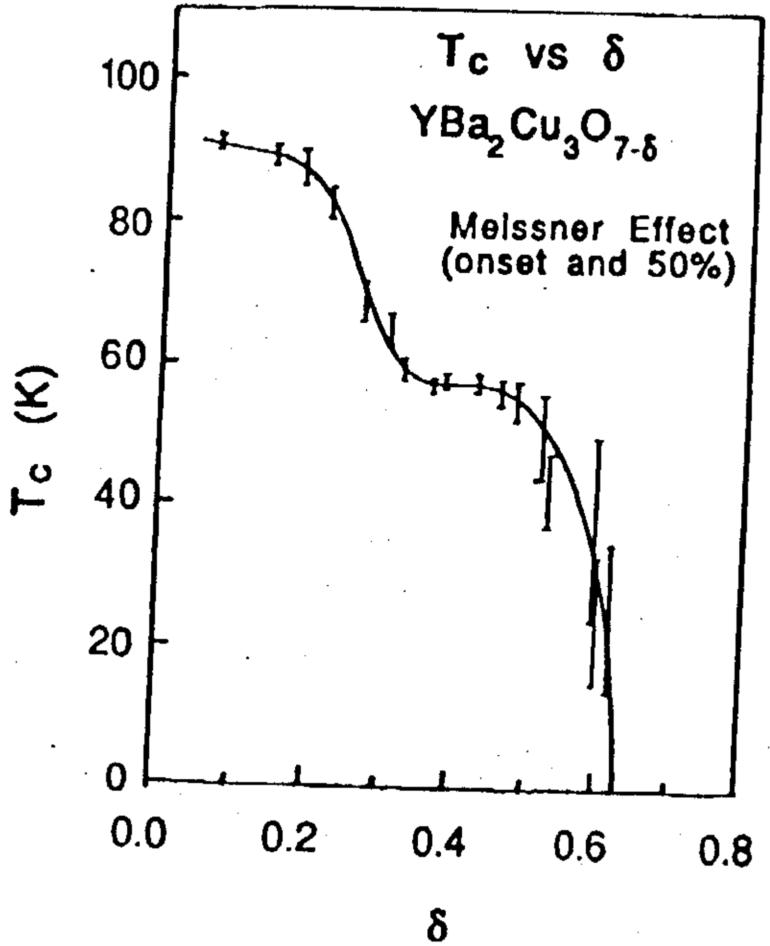
Data analysis :

powder data → Rietveld analysis
single crystal data

Schematic of IPNS



B. W. Veal, J. D. Jorgensen, G. W. Crabtree, W. K. Kwok, A. Umezawa, A. P. Paulikas, L. R. Morss, E. A. Appelman, L. J. Nowicki, L. Nunez, and H. Claus



C. Namgung, J. T. S. Irvine, and A. R. West, Physica C 168, 346 (1990)

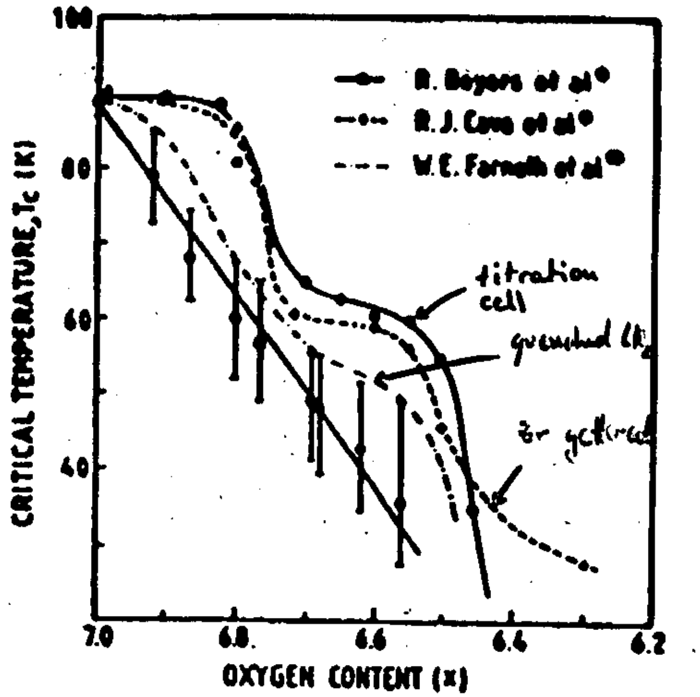
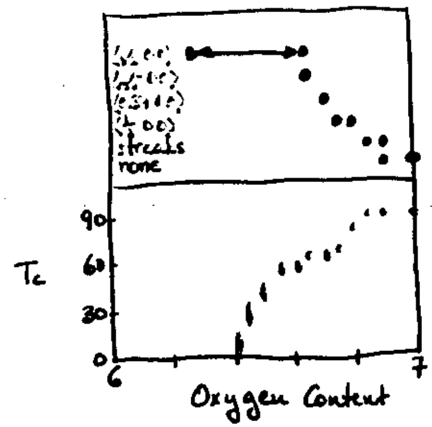


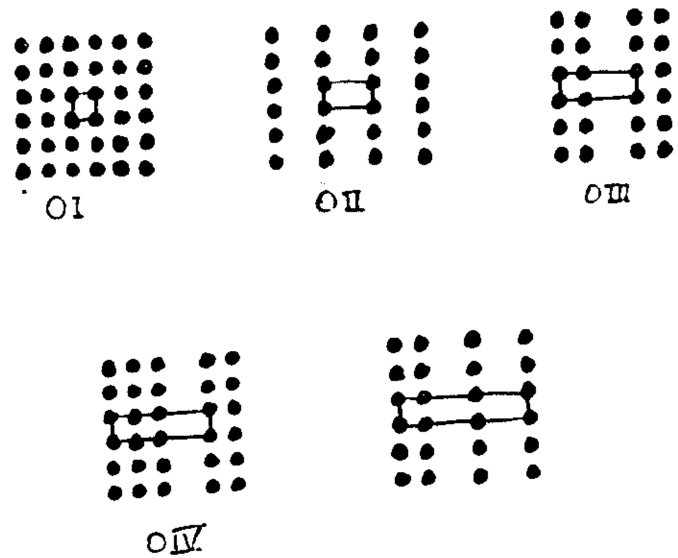
Fig. 3. T_c data, with literature values for comparison. (o) 50% resistive transition, (I) susceptibility onset.

Samples quenched into mercury.

Beyers et al. Nature 340 p619 (1989)



De Fontaine et al. Nature 343 p544 (1990)



R. Kikuchi and J.-S. Choi, Physica C 160, 347 (1989).
D. de Fontaine, G. Ceder, M. Asta, Nature 343, 544 (1990).

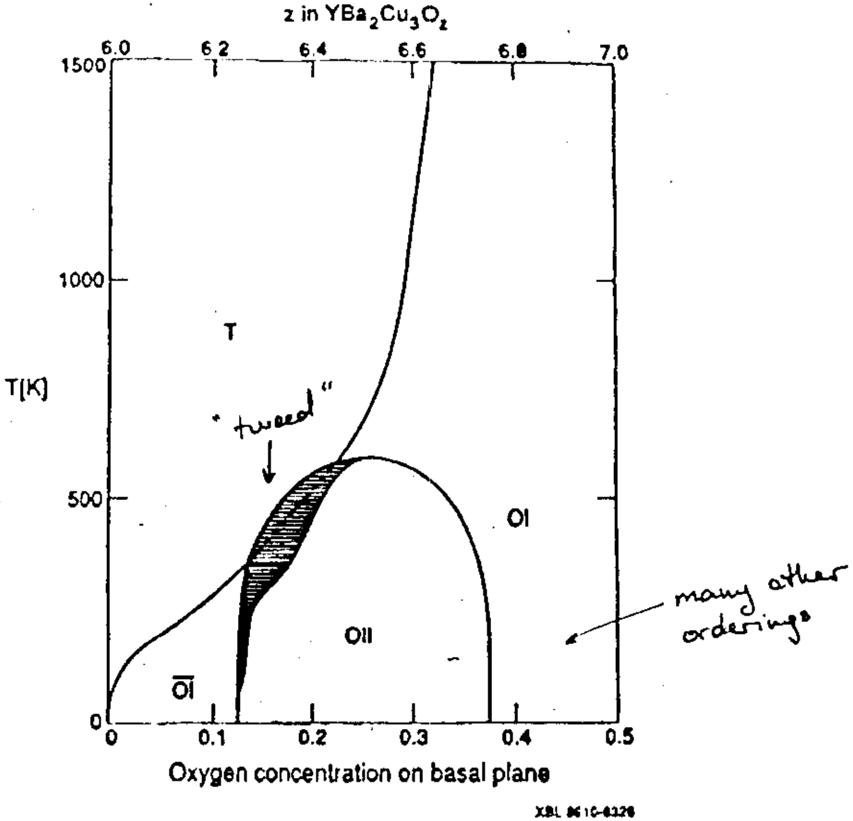
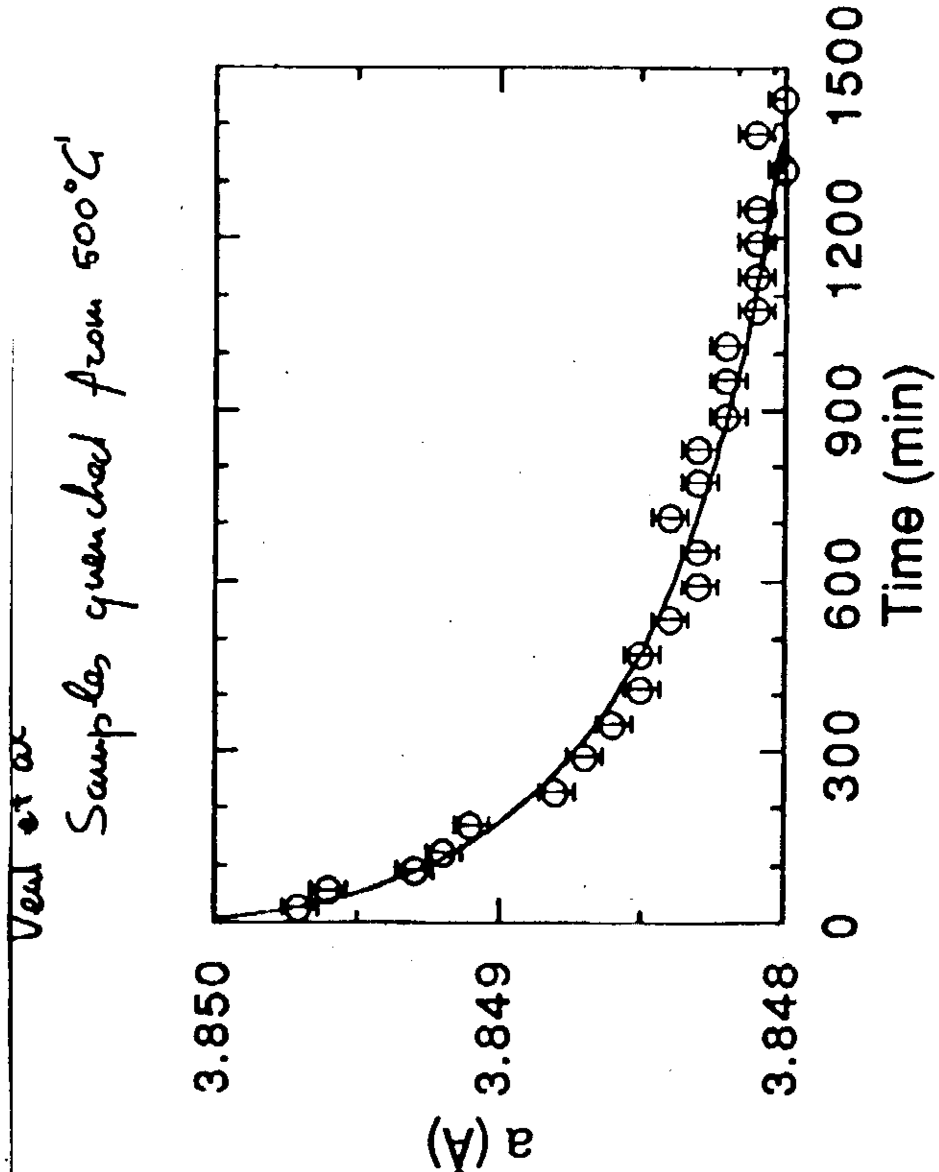
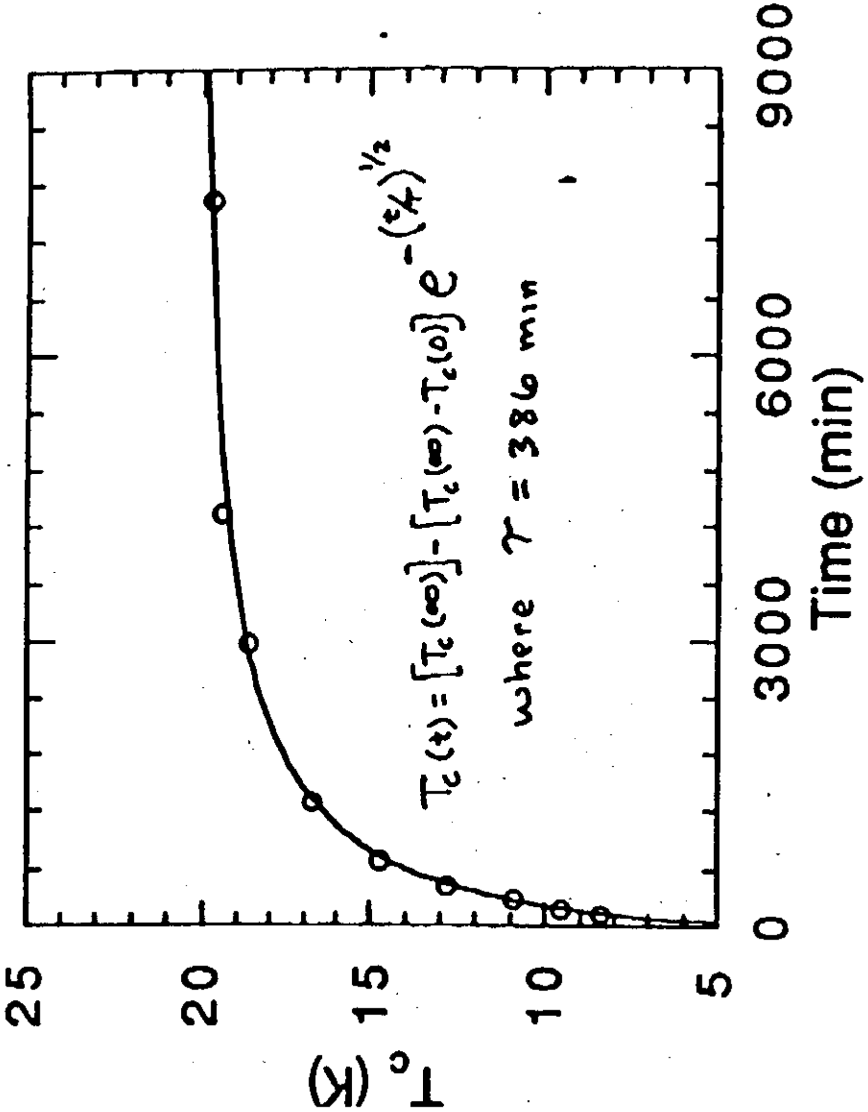


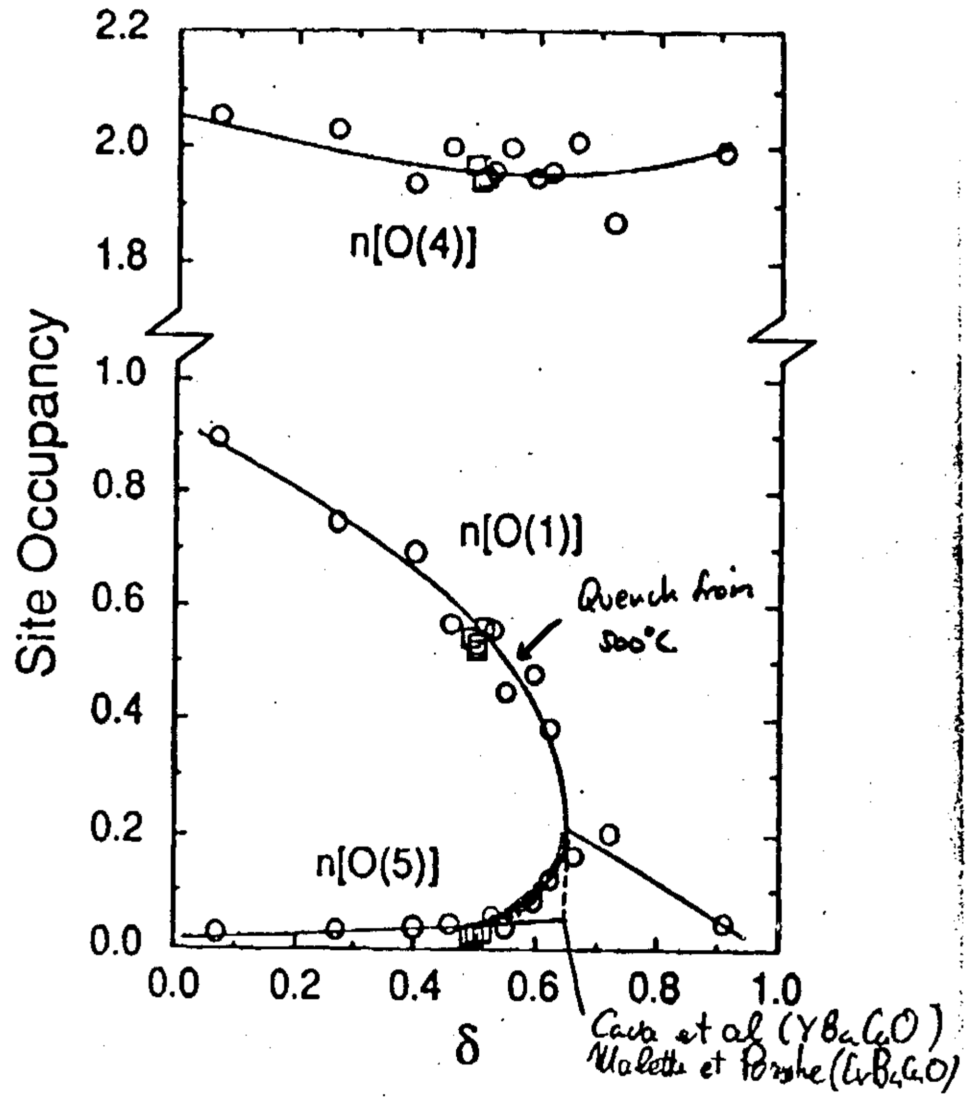
Fig. 3



Veal et al



Time (min)
T_c (K)
$T_c(t) = [T_c(\infty)] - [T_c(\infty) - T_c(0)]\, e^{-(t/\tau)^{1/2}}$
where τ = 386 min



Site Occupancy
δ
n[O(4)]
n[O(1)]
n[O(5)]
Quench from 500°C

Why a new experiment ?

1. Access the low temperature portion of the phase diagram.
2. Try to induce 3-2 ordering visible to neutron diffraction
3. Detect possible 1st order transitions and regions of phase separation
4. Why $ErBa_2Cu_3O_{6+\delta}$?

   Small RE, no solid solution on Ba-site

   T-O transition at low δ well separated from $T_c \to 0$

   1st order $n(OS)$ behavior reported by Maletta et al.

Experiment

Sample Preparation

solid state reaction

$ErBa_2Cu_3O_7$ $\delta = 1$

$\downarrow$ vacuum annealing

$ErBa_2Cu_3O_6$ $\delta = 0$

$\delta = 1$ + $\delta = 0$ sealed in quartz tubes

400°C $\longrightarrow$ 50°C over 2 months

Neutron Powder Diffraction

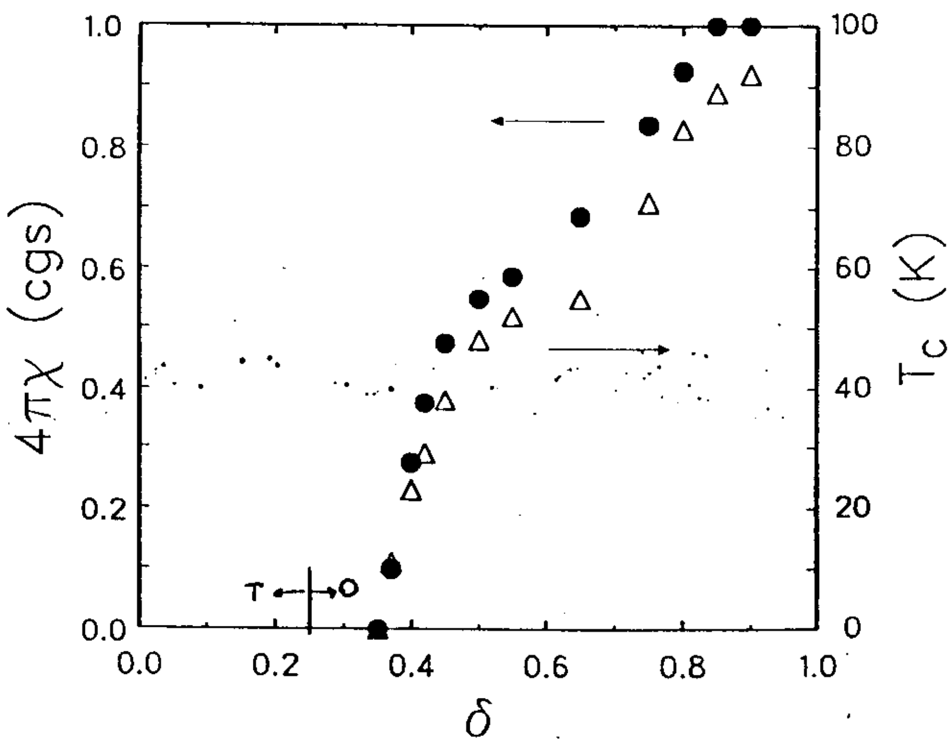
diffraction patterns taken at R.T. on GPPD - IPNS

Rietveld refinement

Oxygen Content + Magnetic Measurements

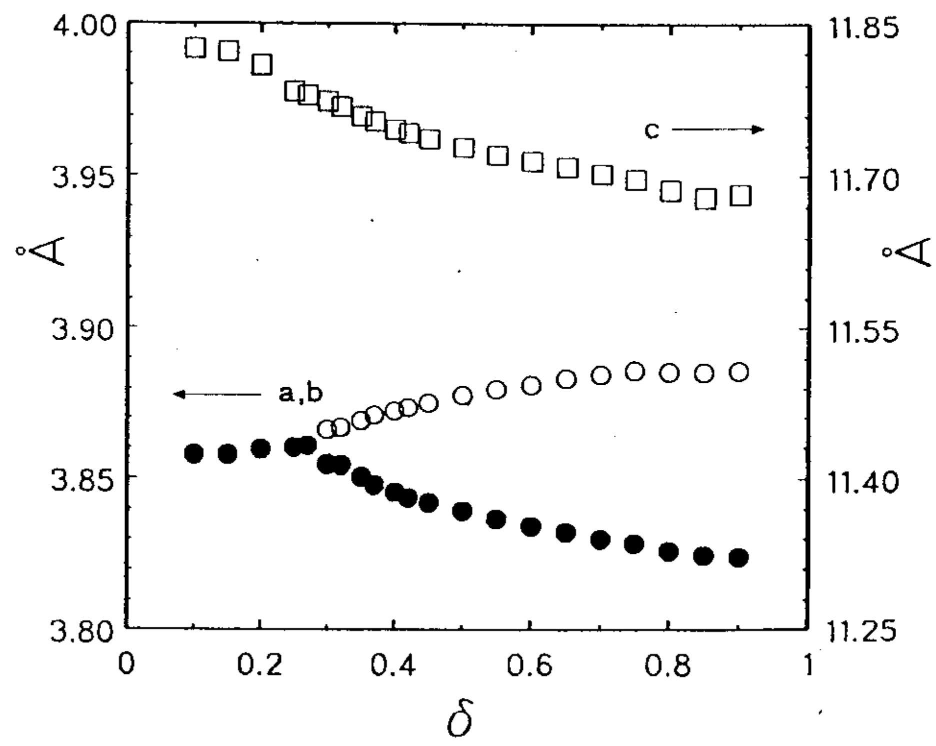
TGA on endpoint compositions other compositions calculated

χ and s.c. volume fraction measured by a.c. susceptibility



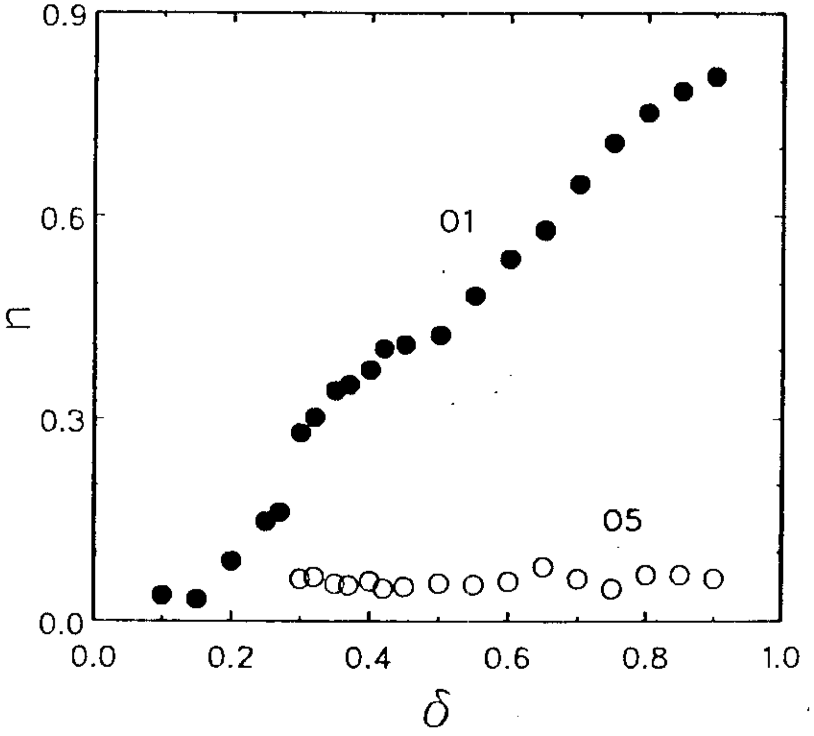
1.0
0.8
0.6
0.4
0.2
0.0
100
80
60
40
20
0
0.0
0.2
0.4
0.6
0.8
1.0
$4\pi\chi$ (cgs)
T_c (K)
T
O
δ

Fig.6

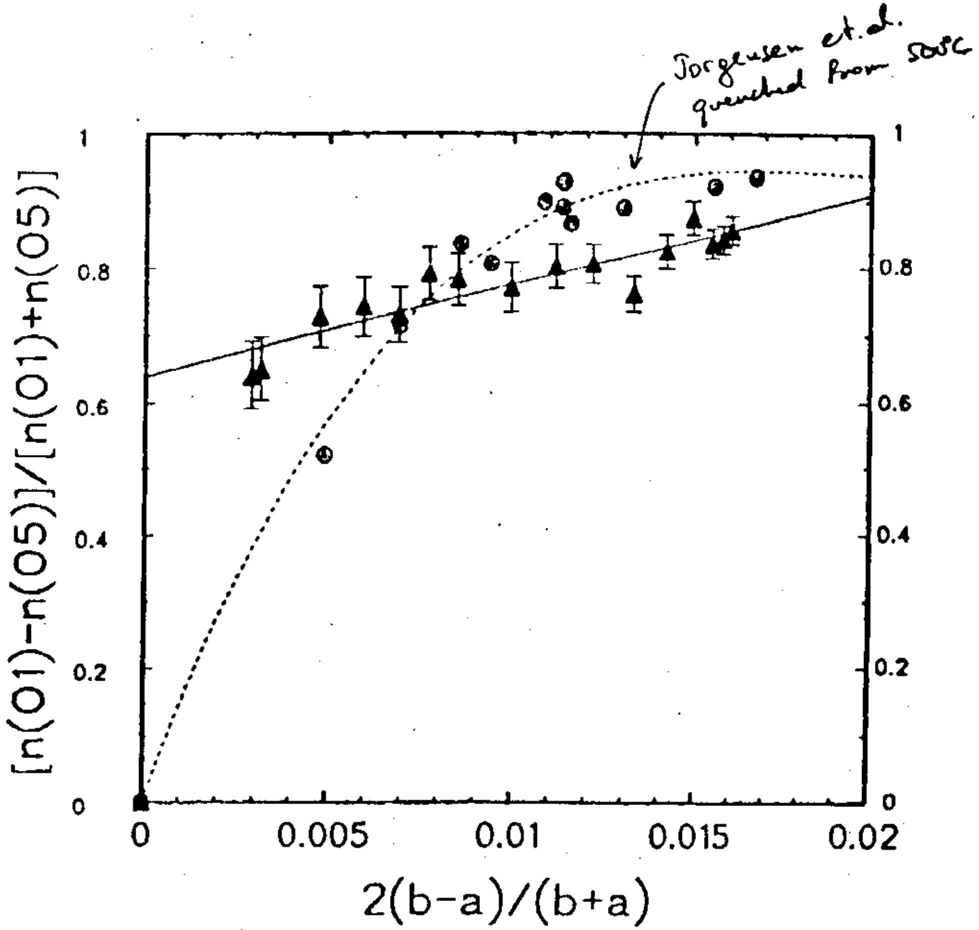


4.00
3.95
3.90
3.85
3.80
11.85
11.70
11.55
11.40
11.25
0
0.2
0.4
0.6
0.8
1
Å
Å
c
a,b
δ

Fig.1



0.9
0.6
0.3
0.0
n
O1
O5
0.0
0.2
0.4
0.6
0.8
1.0
δ



Jorgensen et.al.
quenched from 500C
[n(O1)-n(O5)]/[n(O1)+n(O5)]
1
0.8
0.6
0.4
0.2
0
0
0.005
0.01
0.015
0.02
2(b-a)/(b+a)

Fig.2

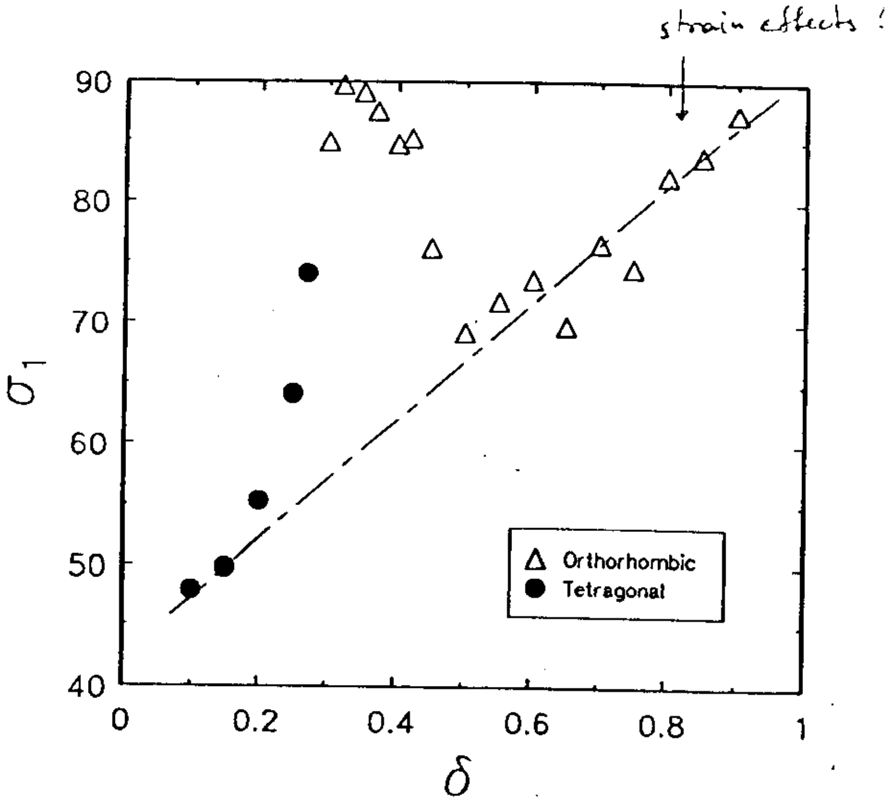

strain effects !
90
80
70
60
50
40
0
0.2
0.4
0.6
0.8
1
σ_1
δ
Orthorhombic
Tetragonal

Fig.3

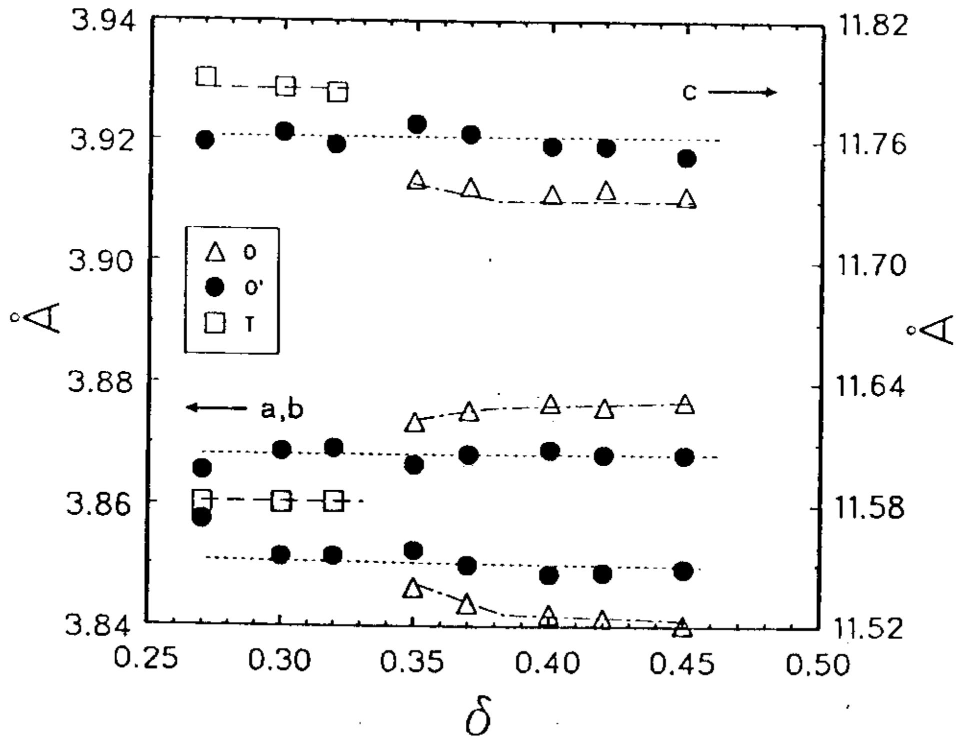

3.94
3.92
3.90
3.88
3.86
3.84
11.82
11.76
11.70
11.64
11.58
11.52
0.25
0.30
0.35
0.40
0.45
0.50
Å
Å
δ
c
a,b
O
O'
T

Fig.4

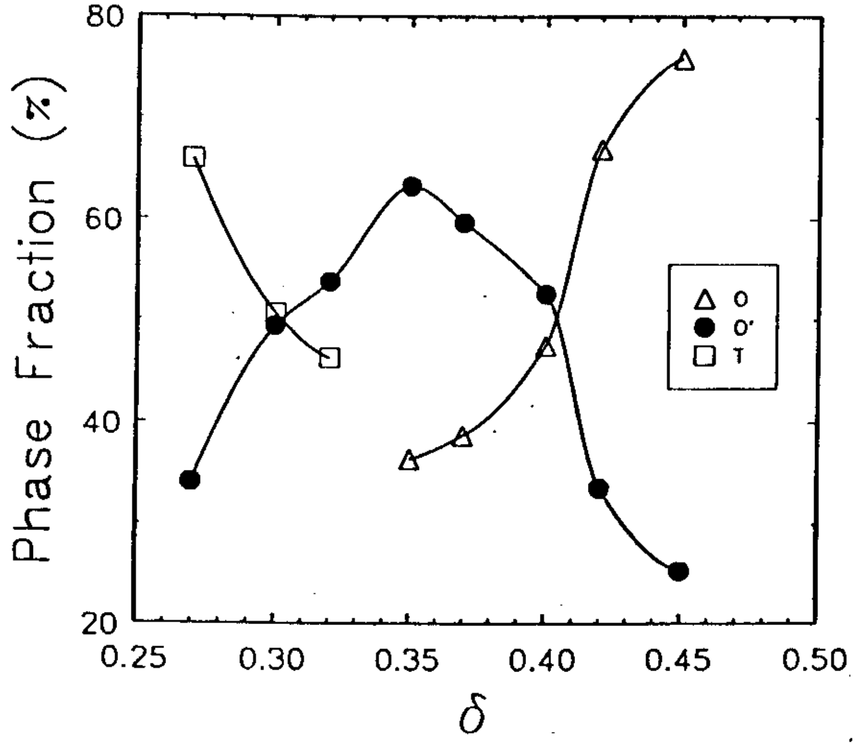


Fig.5

Conclusions

3-D ordering not seen by neutron diffraction

Phase separation at high δ not obvious

Phase separation at low δ is visible
- most likely is "tweed" structure
- could be evidence for 1^{st} order transition between T and O

Planned Experiments

High resolution X-ray diffraction to look at details of line shape and superstructures

Careful new low temperature synthesis to avoid any possible strain broadening which obscures high δ data.

Substitution on Y-site

Rare earths : La Ce Pr Nd Sm Eu Gd Tb
Dy Er Ho Tm (Yb)(Lu)

$T_c \sim 90K$ except for Pr !

Alkaline earths : Ca (Sr)

Substitution on Ba-site

Alkaline earths : (Ca) Sr

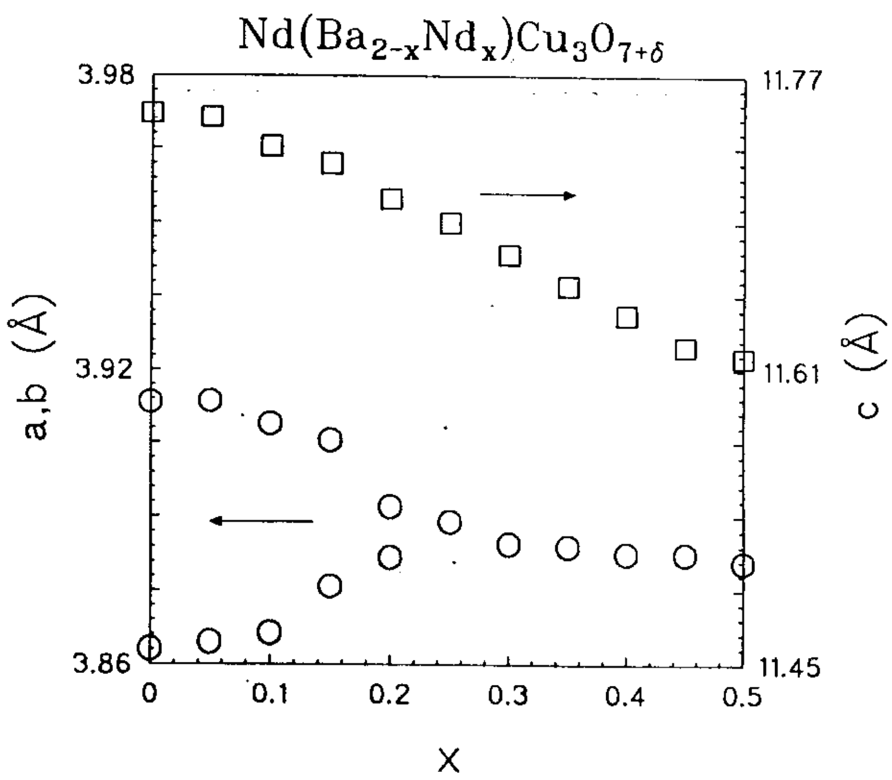
Rare earths : "large" ones only (La, Nd, Pr, Sm, Eu, Gd)

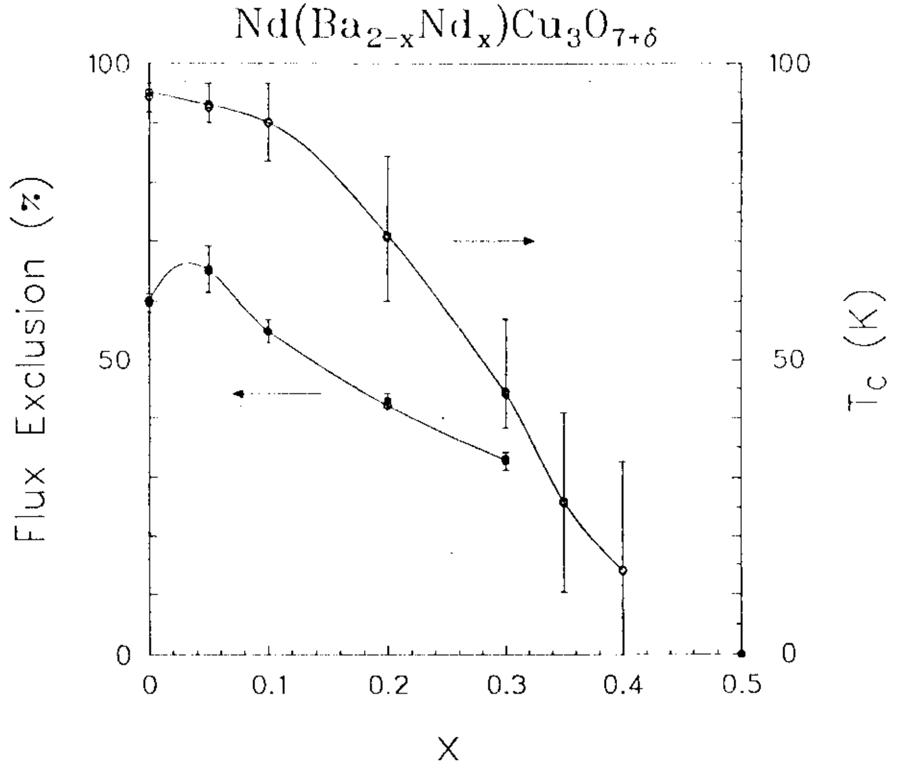
classic case $La_{1.5}Ba_{1.5}Cu_3O_{7+\delta}$

$\Downarrow$

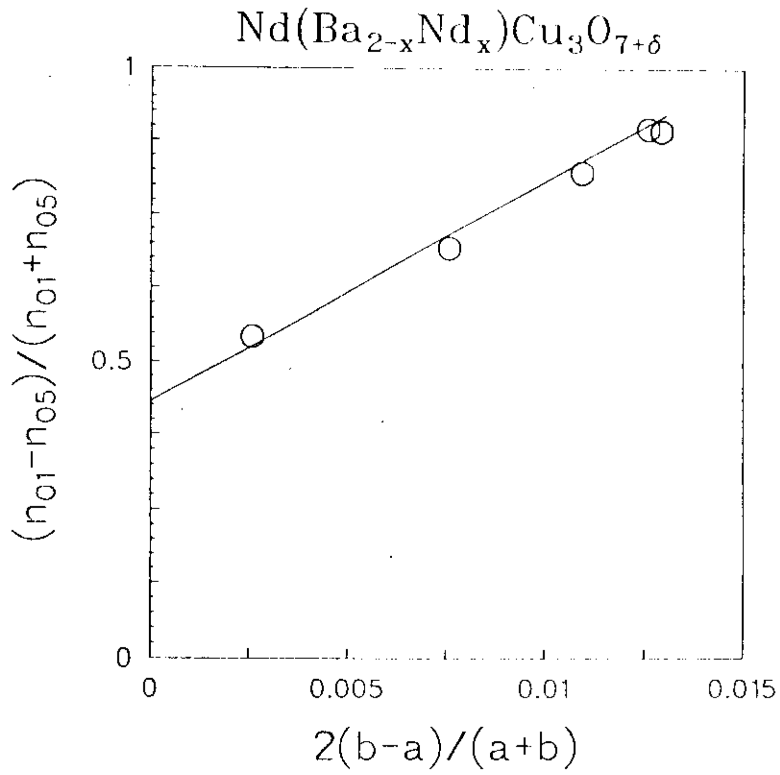
$La(Ba_{1.5}La_{0.5})Cu_3O_{7+\delta}$

Unifying Theme : ionic radius dominates

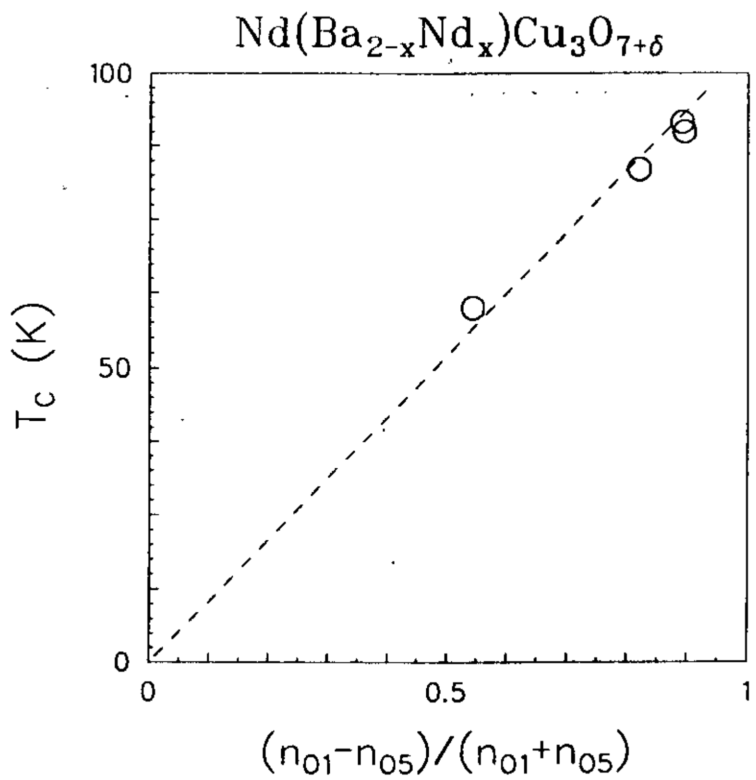




Nd(Ba$_{2-x}$Nd$_x$)Cu$_3$O$_{7+\delta}$
Flux Exclusion (%)
T_c (K)
100
50
0
0
0.1
0.2
0.3
0.4
0.5
X



Nd(Ba$_{2-x}$Nd$_x$)Cu$_3$O$_{7+\delta}$
$(n_{O1}-n_{O5})/(n_{O1}+n_{O5})$
1
0.5
0
0
0.005
0.01
0.015
2(b-a)/(a+b)



Conclusions

Substitutional studies very difficult to interpret

Even neutron diffraction cannot resolve certain questions of structure

Must use complementary methods

Systematics, systematics, systematics

How to do careful substitutional studies on a low budget?

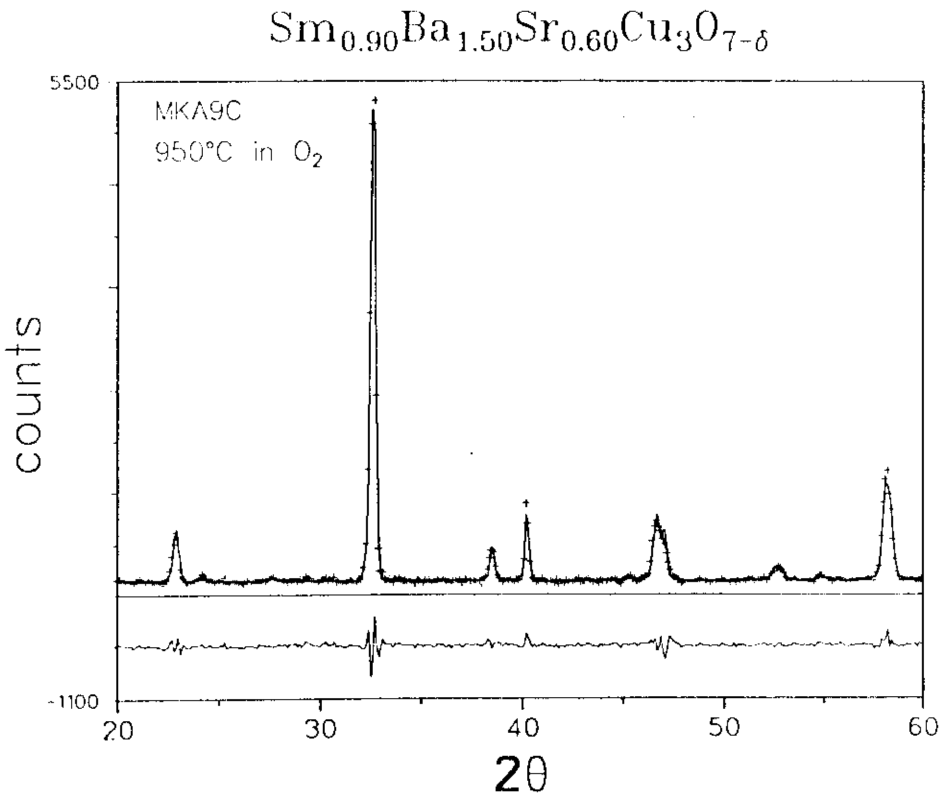
1. Careful sample preparation
   many compositions
   many treatments

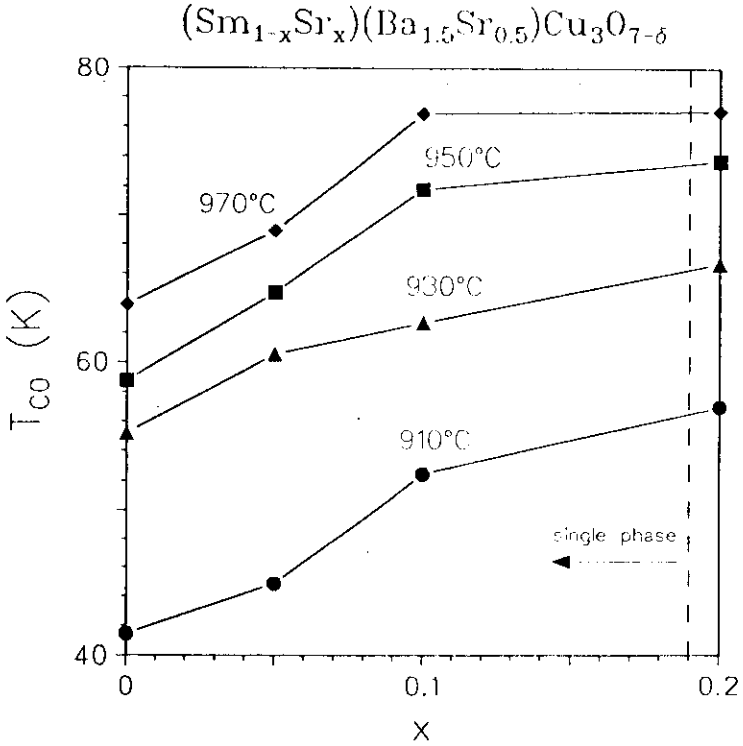
2. X-ray diffraction (at least)
   look for consistent results

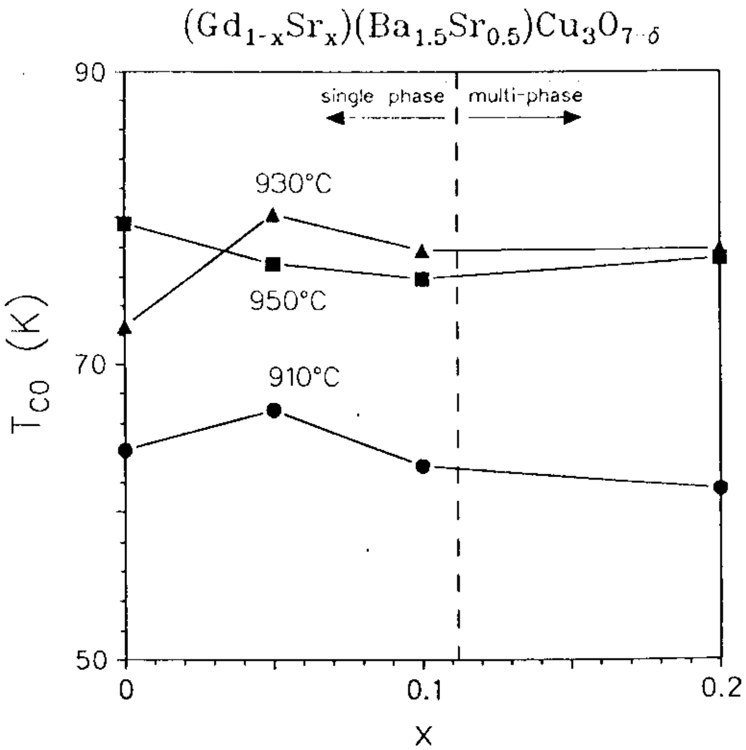
3. Measure oxygen content on "single phase" samples

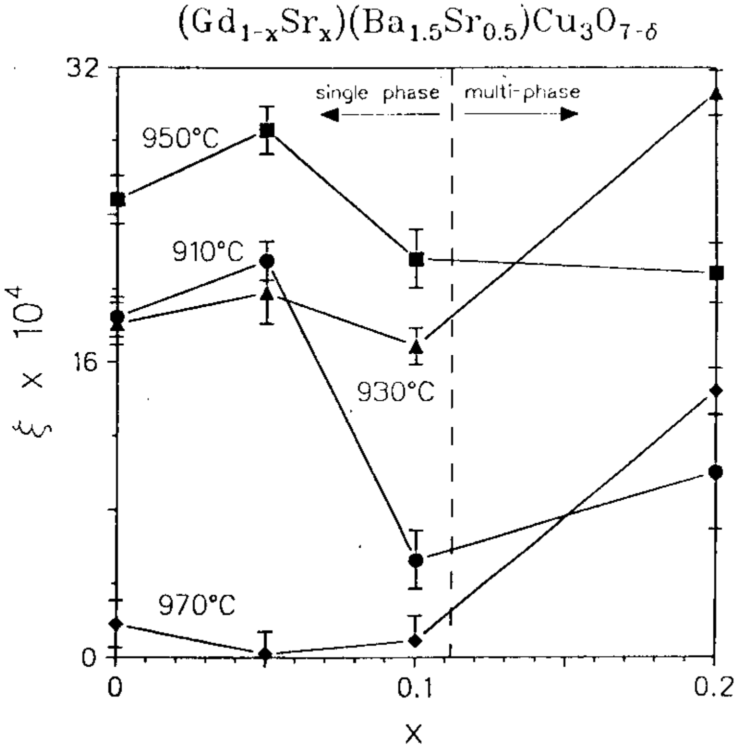
4. Measure ρ vs T, $\underline{\underline{T_{c0}}}$, χ_{ac} (if possible)

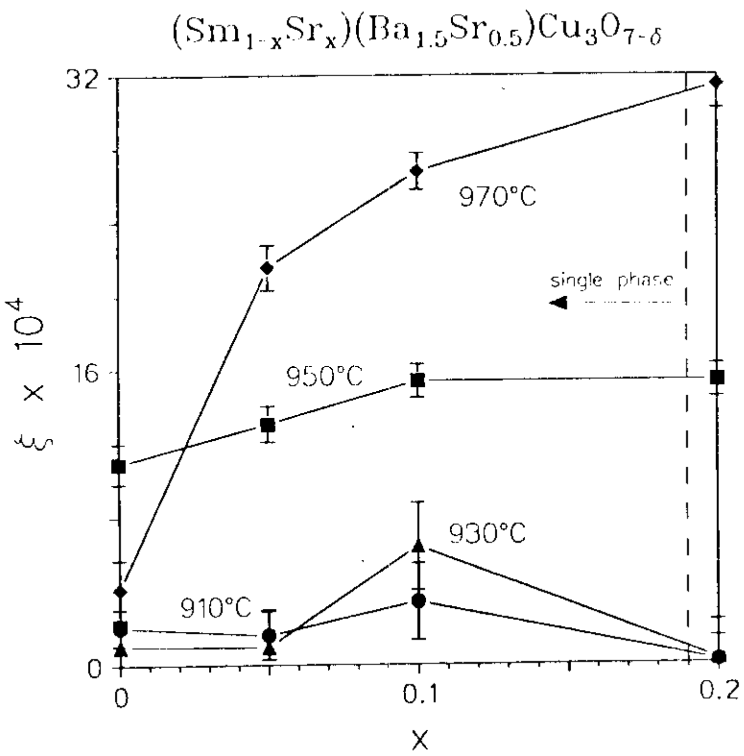
Example: Sr substitution on Y-site by simultaneous substitution on Ba-site.


$Sm_{0.90}Ba_{1.50}Sr_{0.60}Cu_3O_{7-\delta}$
5500
MKA9C
950°C in O_2
counts
-1100
20
30
40
50
60
2θ

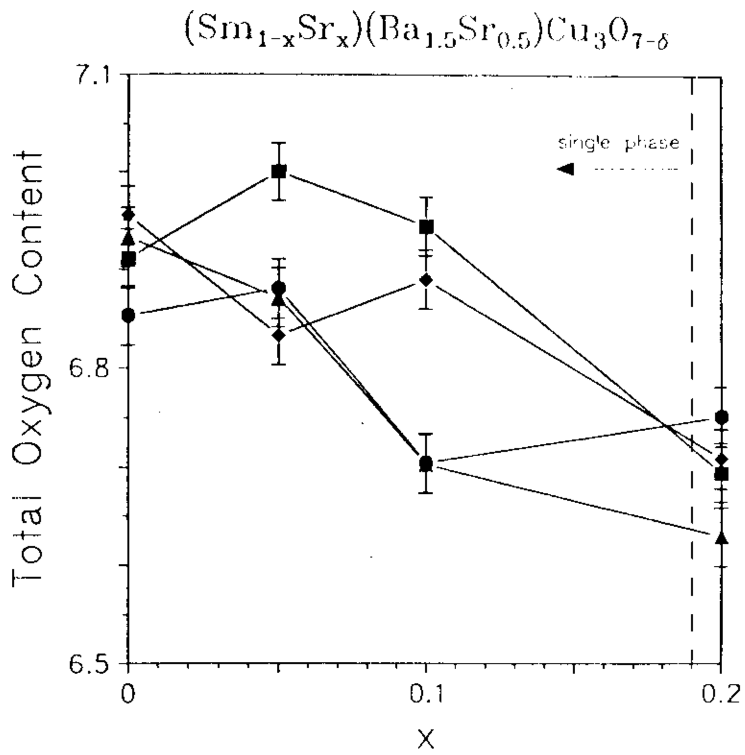

$(Sm_{1-x}Sr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_{7-\delta}$
80
60
40
T_{co} (K)
970°C
950°C
930°C
910°C
single phase
0
0.1
0.2
x


(Gd1-xSrx)(Ba1.5Sr0.5)Cu3O7-δ
single phase
multi-phase
930°C
950°C
910°C
TCO (K)
90
70
50
0
0.1
0.2
x

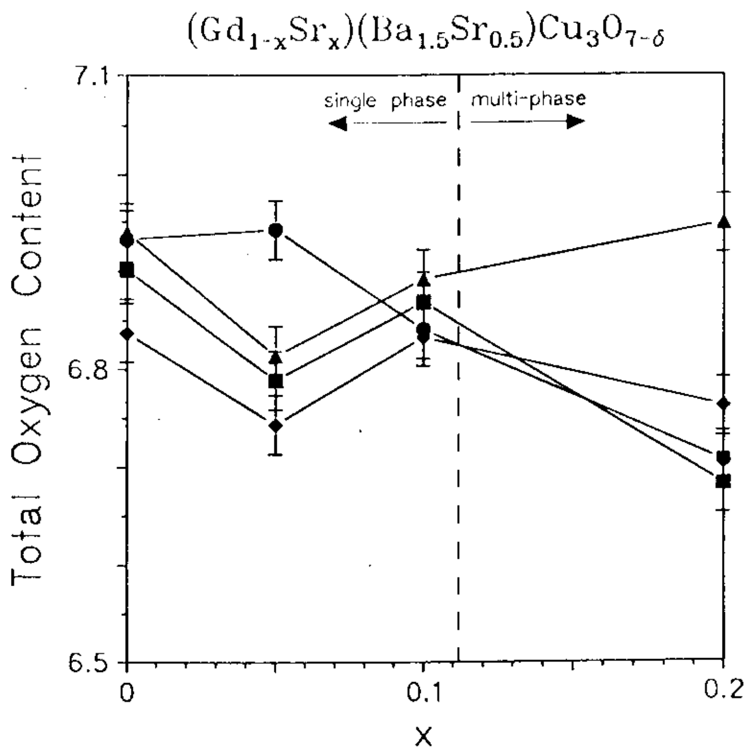

(Gd1-xSrx)(Ba1.5Sr0.5)Cu3O7-δ
single phase
multi-phase
950°C
910°C
930°C
970°C
ξ x 10^4
32
16
0
0
0.1
0.2
x



$(Sm_{1-x}Sr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_{7-\delta}$
32
16
0
$\xi \times 10^4$
970°C
950°C
930°C
910°C
single phase
0
0.1
0.2
X



$(Sm_{1-x}Sr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_{7-\delta}$
7.1
6.8
6.5
Total Oxygen Content
single phase
0
0.1
0.2
X



(Gd1-xSrx)(Ba1.5Sr0.5)Cu3O7-δ
7.1
6.8
6.5
Total Oxygen Content
single phase
multi-phase
0
0.1
0.2
X