INTERNATIONAL ATOMIC ENERGY AGENCY
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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR/455 - 27

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

12 - 30 MARCH 1990

HREM OF SUPERCONDUCTING CERAMICS

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HREM of Superconducting Ceramics

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Electron Microscopy of High Tc Superconductors

Electron Microscopy ??

a) "big lens"

b) beam - specimen interaction

High Tc Superconductors ??

- specific problems

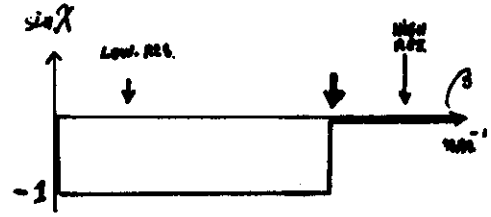
1. $YBa_2Cu_3O_{7-\delta}$
2. $YBa_2Cu_3O_8$
3. BSCCO, TBCCO
4. PSYCCO
5. $Bi(Ba\text{-}K)O_3$

G. Van Tendeloo

IMAGE FORMATION

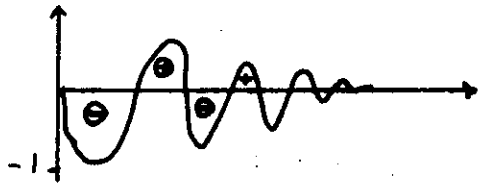
$$\psi(x,y) = \mathcal{F}\left[Q(u,v)\, e^{-i\chi(u,v)} \right]$$

"THE WAY REALITY IS DISTORTED BY THE MICROSCOPE ?"



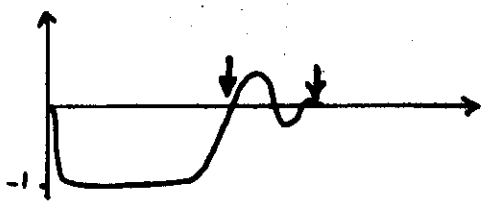
"IDEAL MICROSCOPE"

$$I(x,y) = 1 - \varphi(x,y)$$



"REAL MICROSCOPE - GENERAL"

$I(x,y)$ = VERY COMPLEX... (FUNCTION OF Δf, ...)



"REAL MICROSCOPE - SCHERZER"

$\sin\chi \approx 1$

$I(x,y) \approx 1 - \mathrm{cte}\ \varphi(x,y)$

⊖ NO DETAILED ATOM POSITIONS

NO INTERATOMIC DISTANCES

ONLY PROJECTED INFORMATION

⊕ • FAST

• NO "SINGLE CRYSTALS" REQUIRED

• REAL SPACE ⊕ RECIPROCAL SPACE INFO

• DETECTION OF IMPERFECTIONS
(on atomic scale)

• SMALL AMOUNTS SECONDARY PHASES
(< 10nm !)
→ structure (unitcell)
→ ≈ composition
→ relationship to matrix

E.M. of $YBa_2Cu_3O_{9-\delta}$

- ϕ 2.3 - 3 mm
- thickness < 200 nm EM
  < 20 nm HREM

How ?

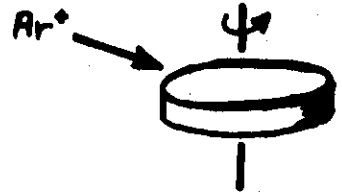
① crushed material

small flakes on a grid

⊕ good for HREM

⊖ no | inter-domain | relationship
| inter-grain |

② ion beam thinned material



⊕ inter grain, domain size, habit pla

⊖ ! artifacts (e.g. amorphisat

ELECTRON MICROSCOPY

⊖ NO DETAILED ATOM POSITIONS

NO INTERATOMIC DISTANCES

ONLY PROJECTED INFORMATION

⊕ • FAST

• NO 'SINGLE CRYSTALS' REQUIRED

• REAL SPACE ⇔ RECIPROCAL SPACE INFO

• DETECTION OF INHOMOGENEITIES

(on a small scale)

• SMALL AMOUNTS, UNKNOWN PHASES

(< 10 nm)

→ structure (+ surface)

→ ± composition

→ relationship to matrix

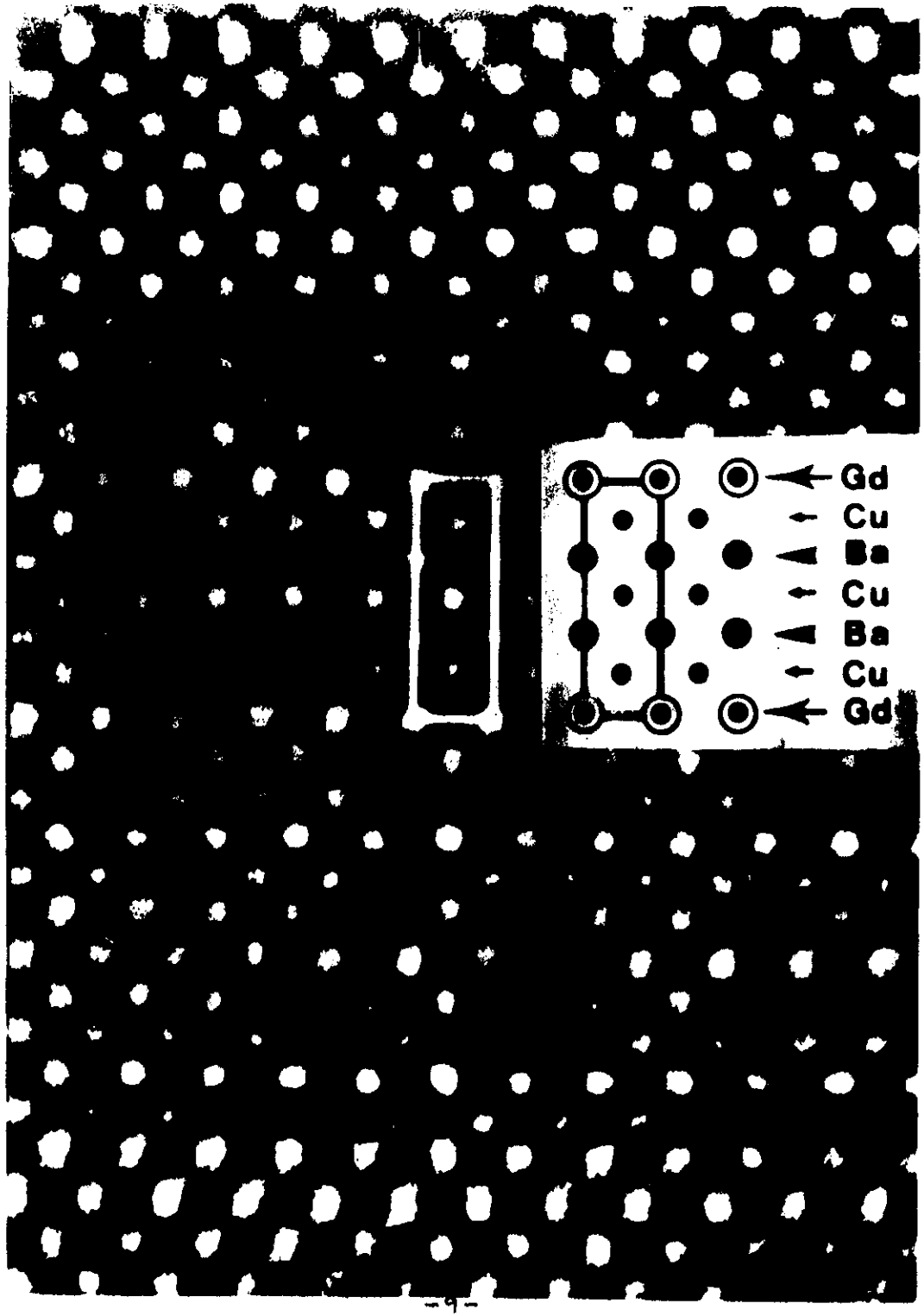
Y-Ba-Cu-O

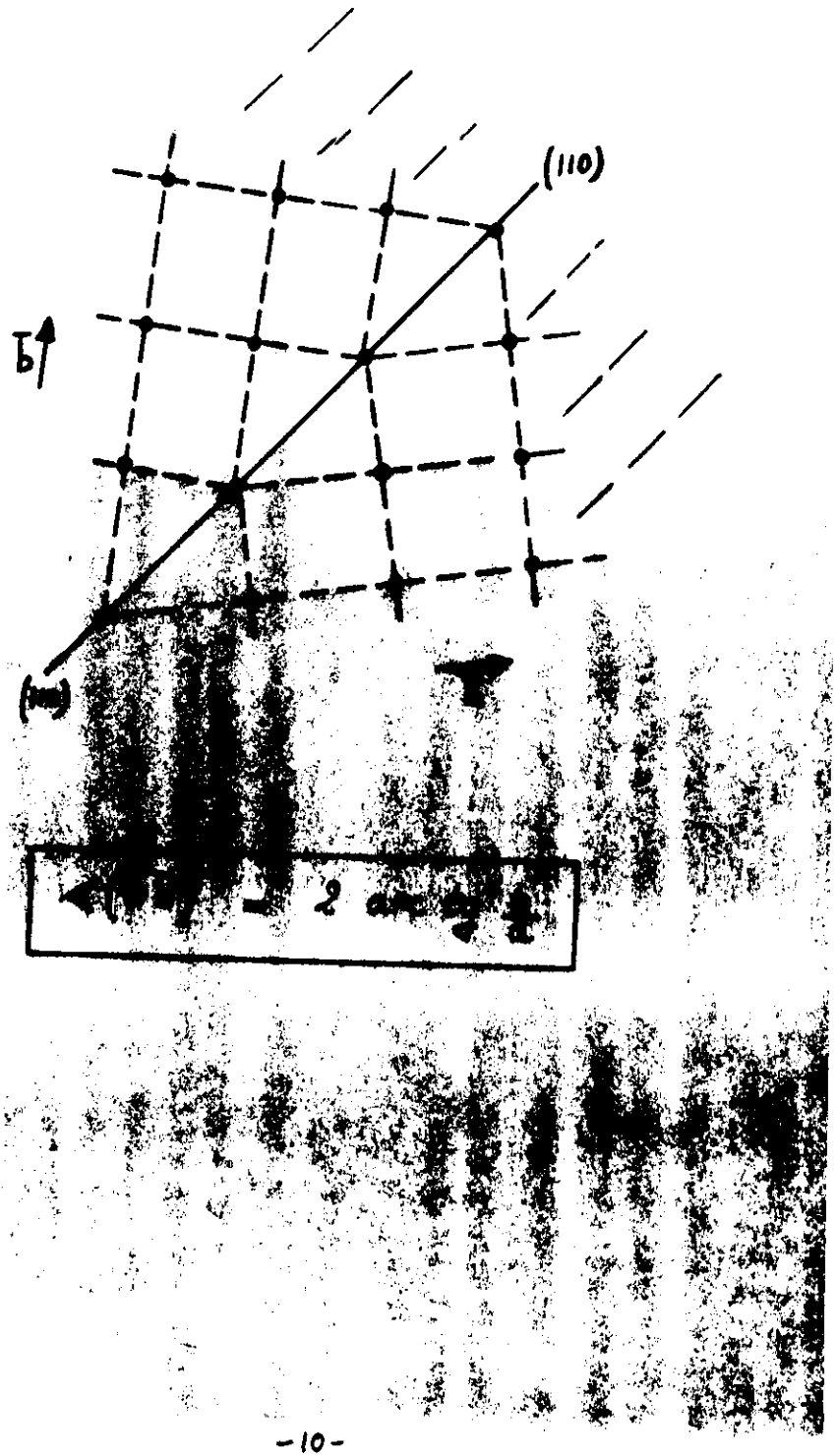
A. $YBa_2Cu_3O_{7-\delta}$

- structure of the (110) twins
- the influence of oxygen

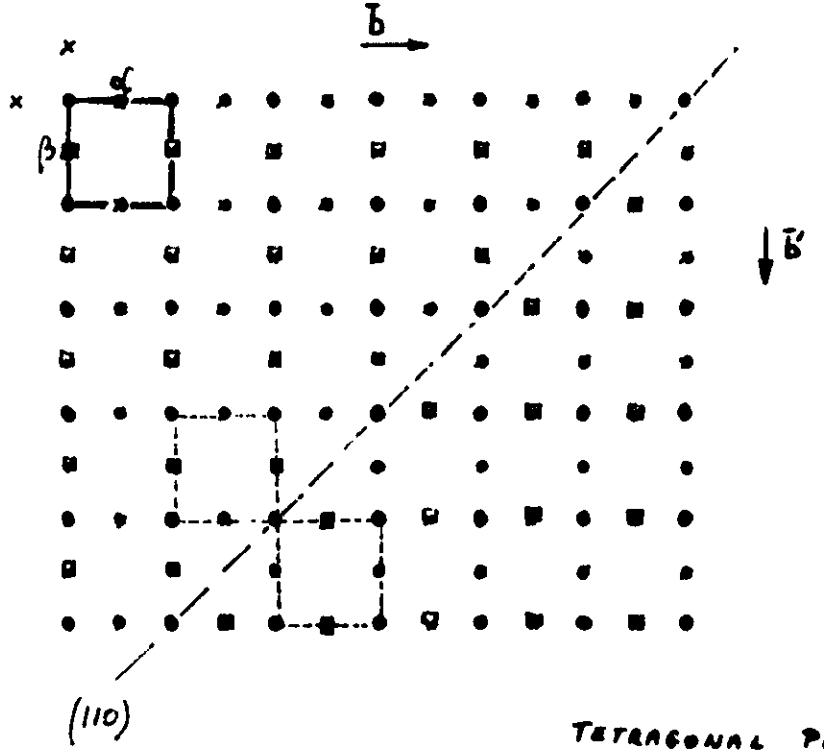
  O I → $2a_o$ → (na_o) → $2\sqrt{2} \times 2\sqrt{2}$ → cubic
- the 60K plateau at $O_{6.5}$-$O_{6.6}$ (K.U. Leuven)

  (Argonne Nat. Lab.)
- the $2\sqrt{2} \times 2\sqrt{2}$ structure
- heavy ion irradiation (Orsay)
- Fe - doped 1-2-3 (ULB Bruxelles)


Gd
Cu
Ba
Cu
Ba
Cu
Gd


(110)
b

Cu - O plane configuration in $YBa_2Cu_3O_{7-\delta}$



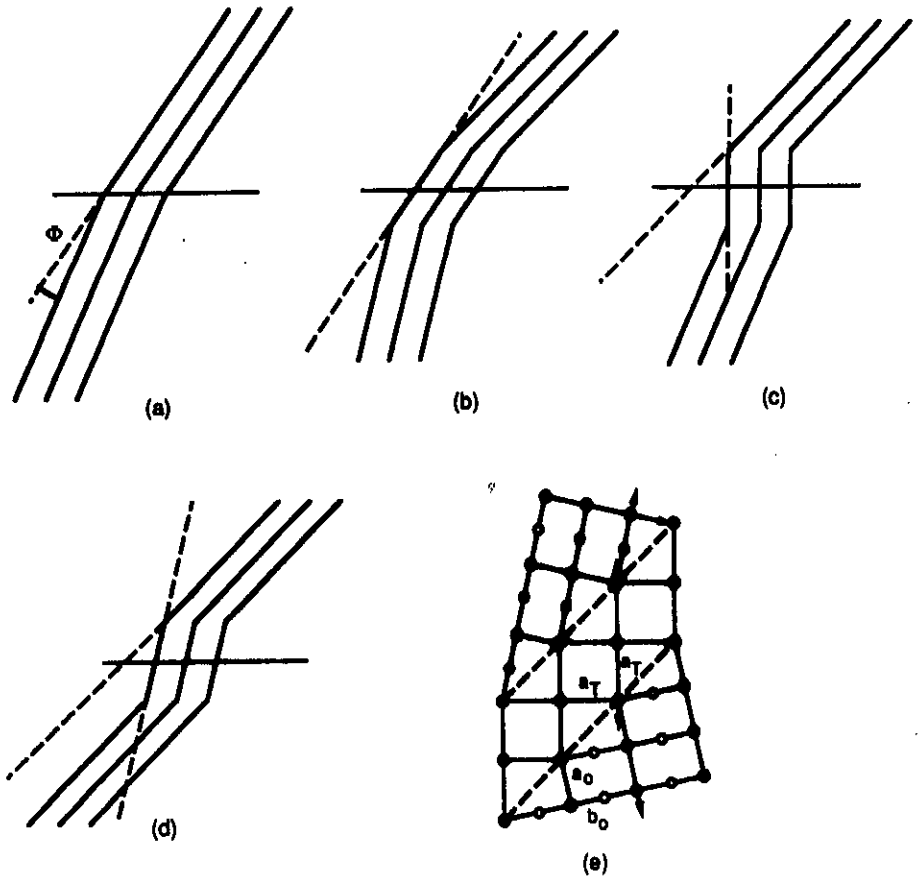
TETRAGONAL PHASE

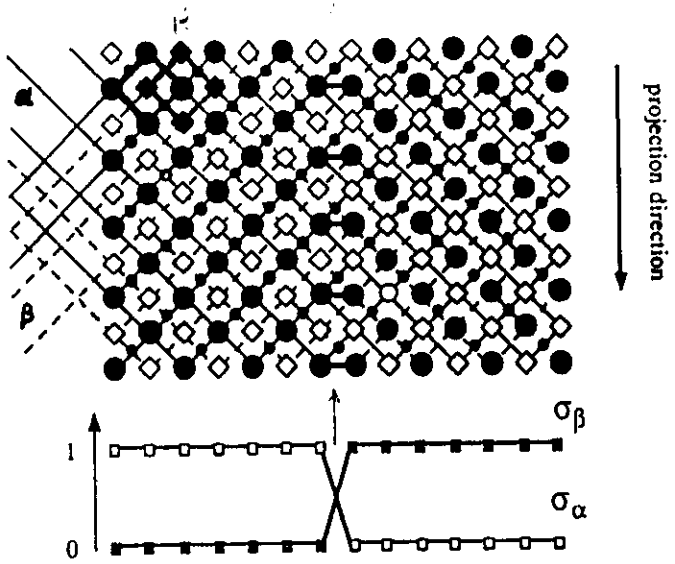
ORTHORHOMBIC PHASE

a = 0.382 nm

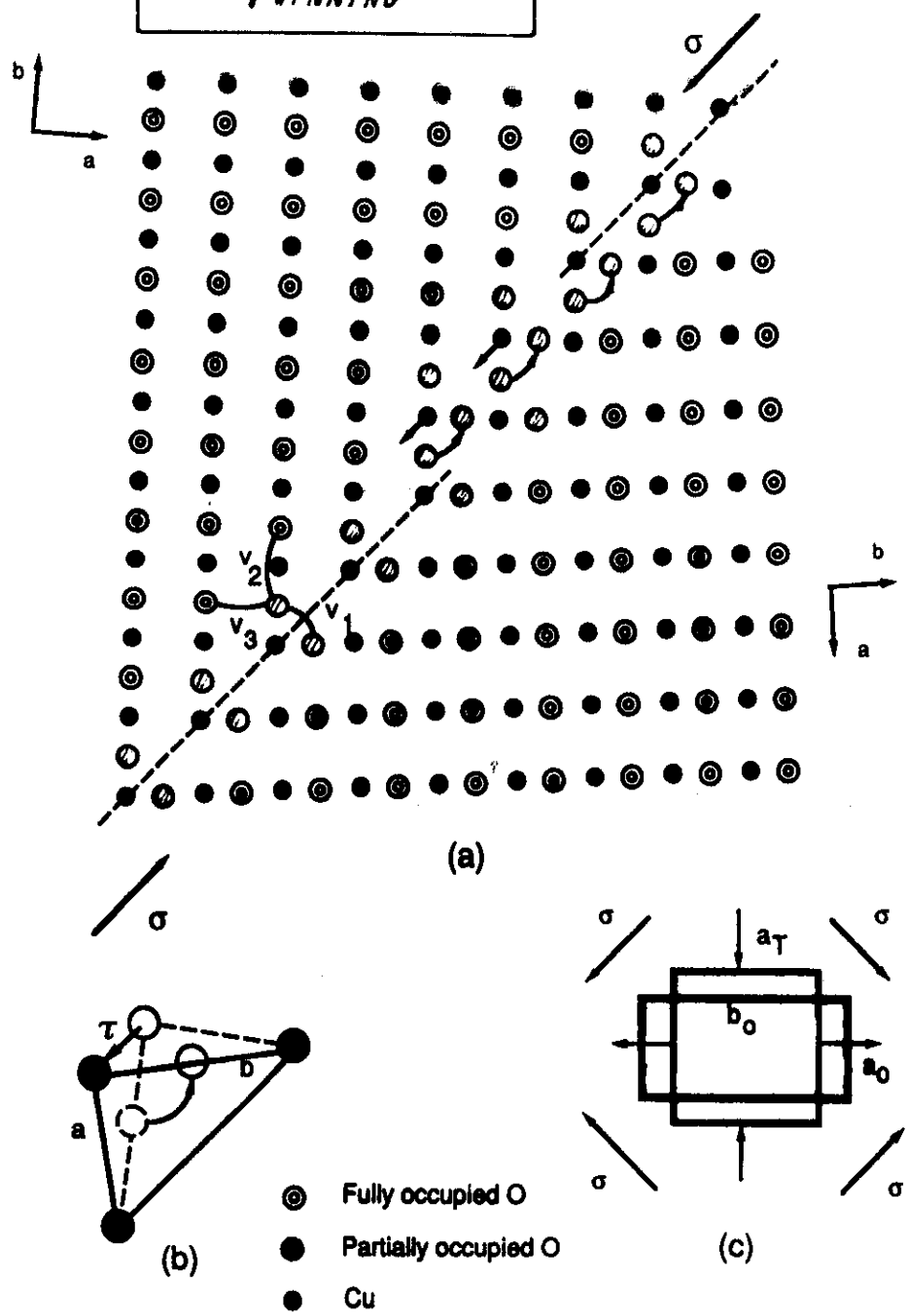
b = 0.389 nm

c = 0.167 nm





"SYNCHRO-SHEAR" TWINNING



Diffuse Interfaces

1. HREM: • NO tetragonal region

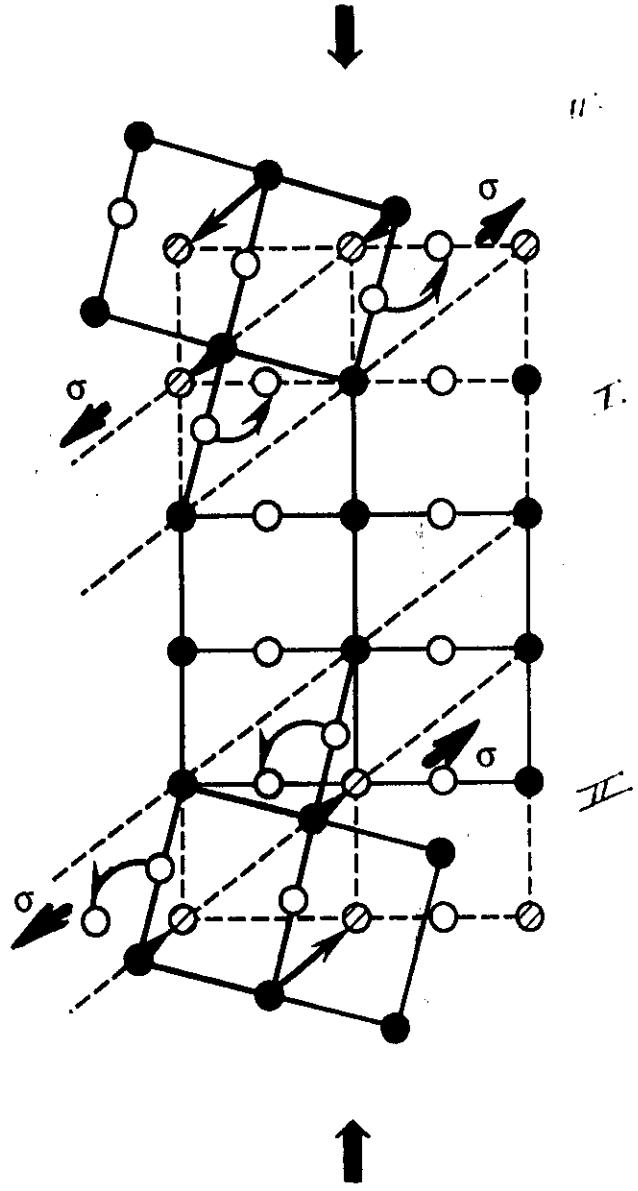
2. Diffraction: orthorhomb. smaller than in 0_7

3. Monte Carlo: vacancies at the interface

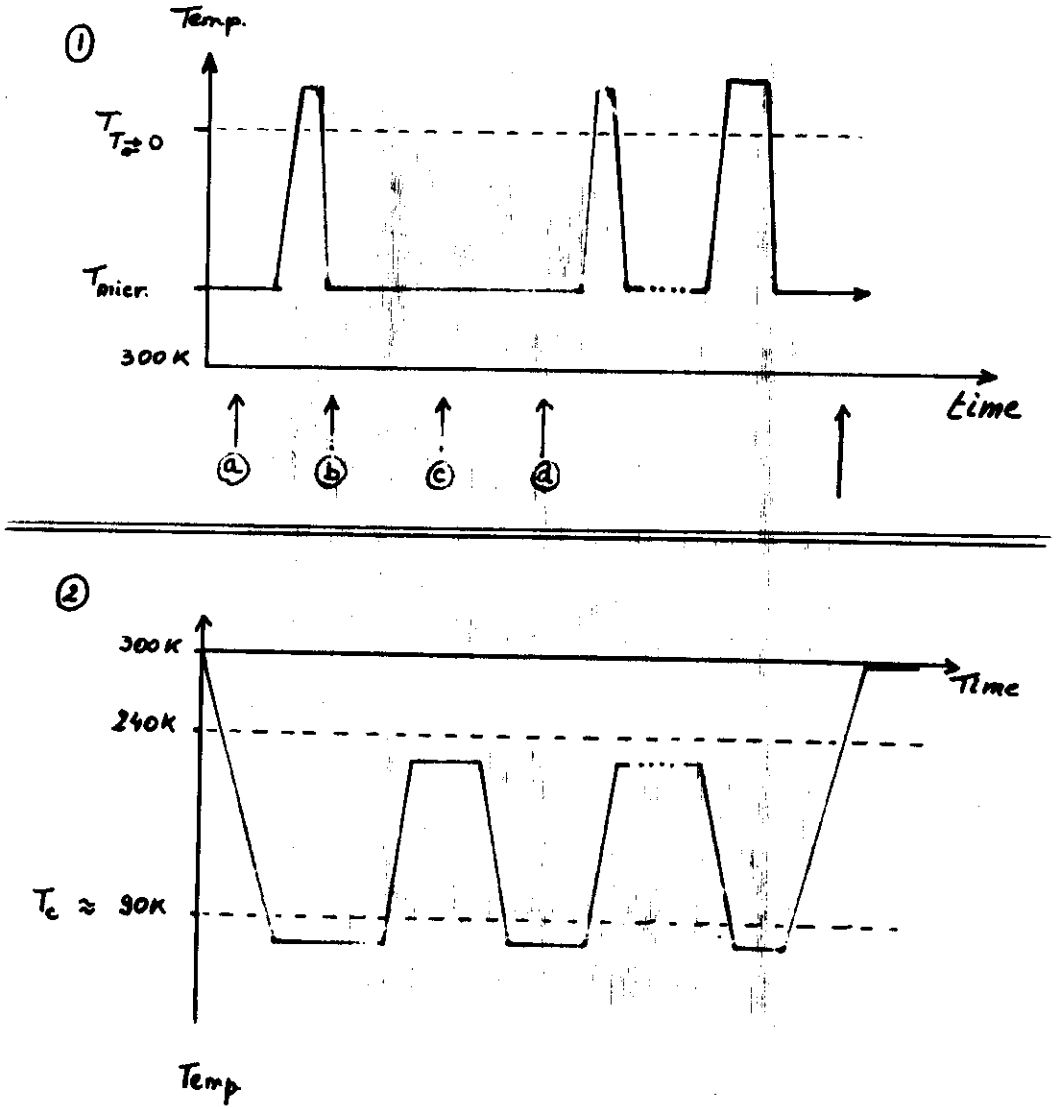
4. HREM simulations: curved interfaces

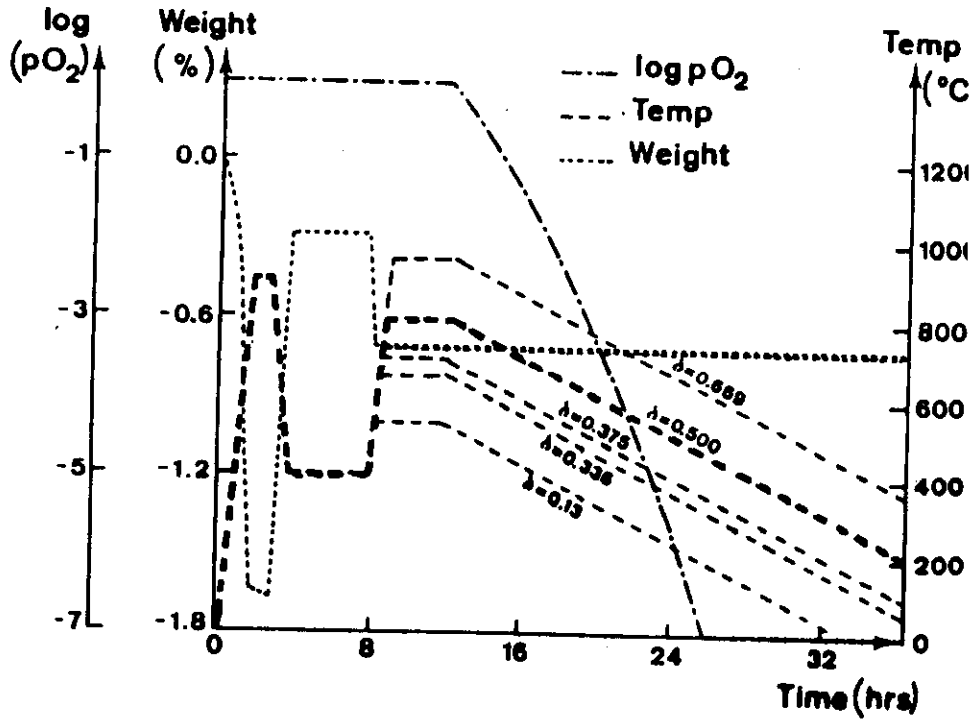
TWINS, NOT EXACTLY IN (110), WITH LOCAL OXYGEN DEFICIENCY

DETWINNING UNDER STRESS



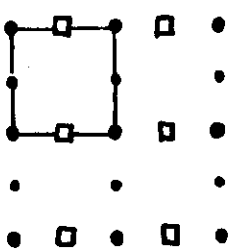
IN SITU EXPERIMENT



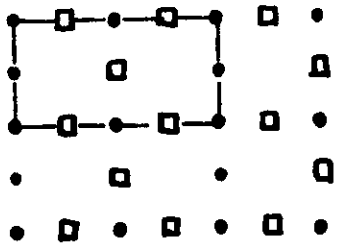


H. Varweij
W.H.M. Broeglink
"Philips" Eindhoven

$YBa_2Cu_3O_x$



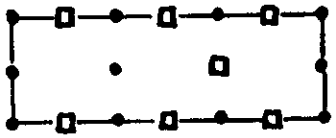
x = 7



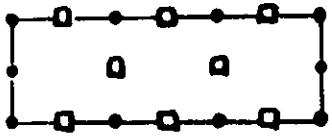
x = 6.5

$2a_o$

O_{II}

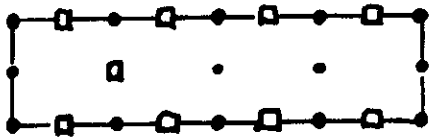


x = 6.67

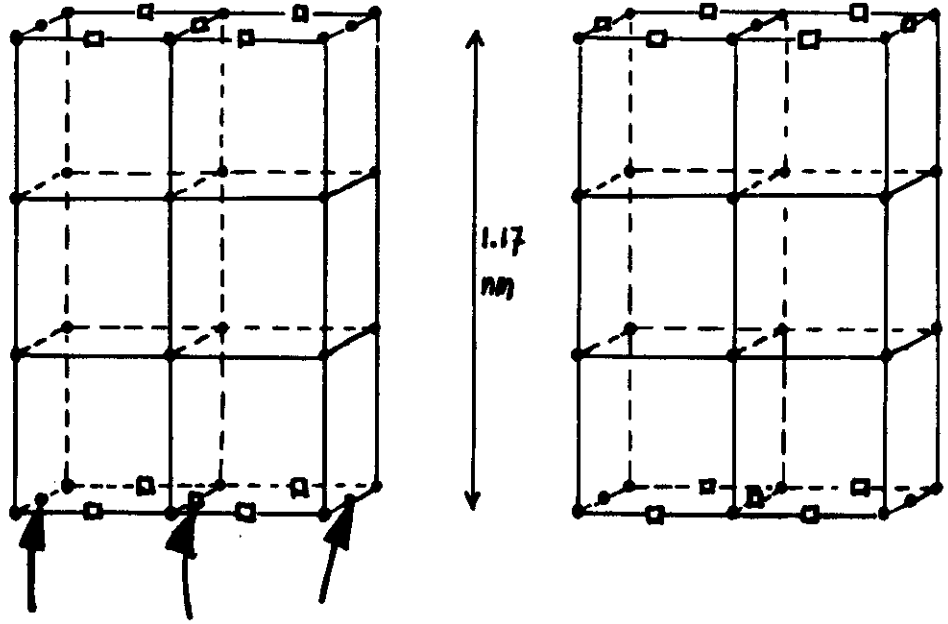


x = 6.35

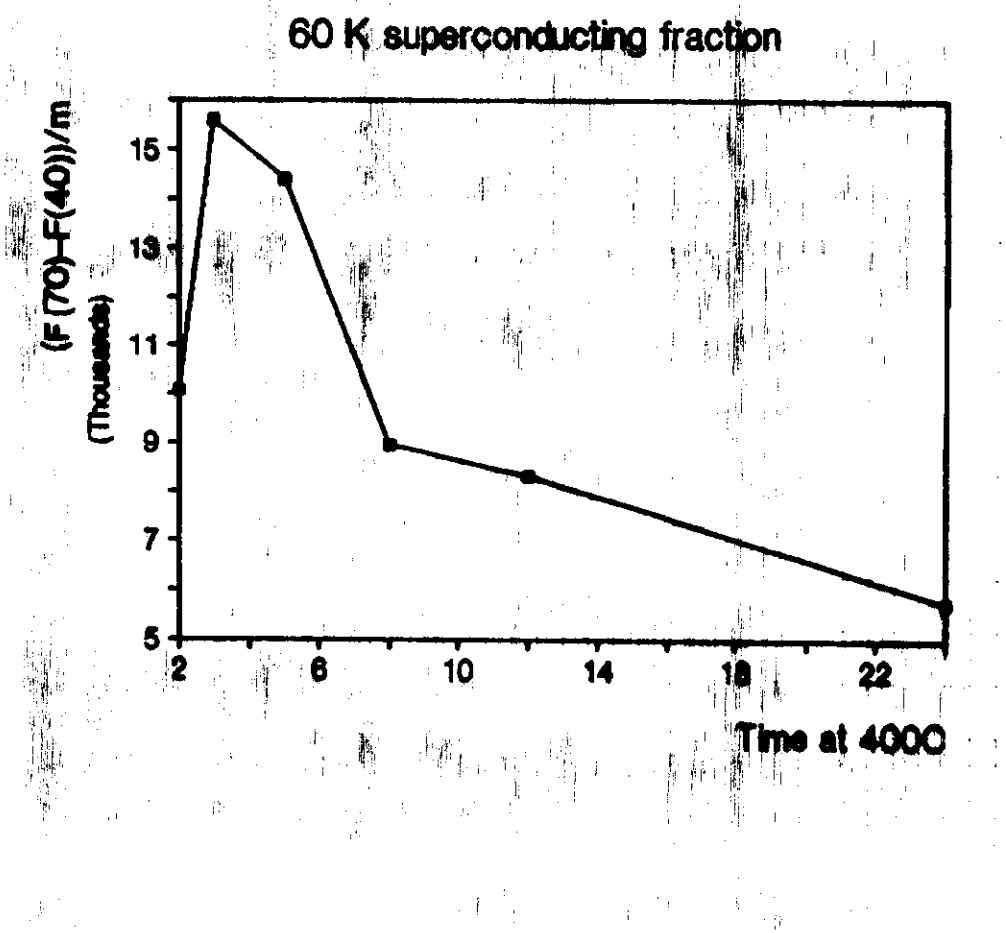
na_o



x = 6.75



$YBa_2Cu_3O_{6.5}$



The $2\sqrt{2} \times 2\sqrt{2}$ structure

Composition: $O_{6.25}$-$O_{6.0}$

Symmetry: P4b2 (90)

or $P4_22$ (117)

STRUCTURE:

a) oxygen ordering

1) In the CuO_{1-x} plane → $O_{6.5}$

2) + In the BaO plane → $O_{6.25}$-

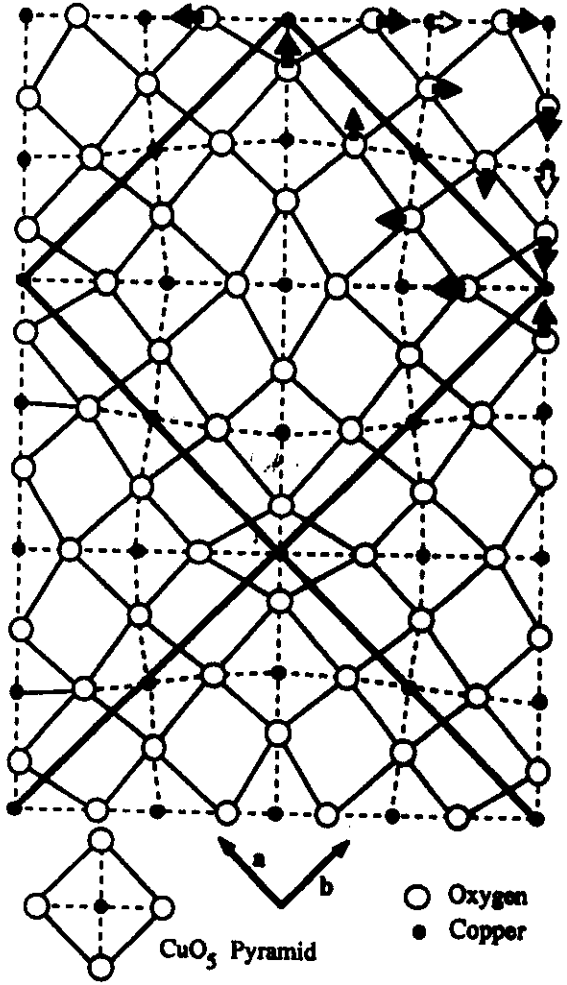
BUT : E.D. INTENSITIES DO NOT FIT

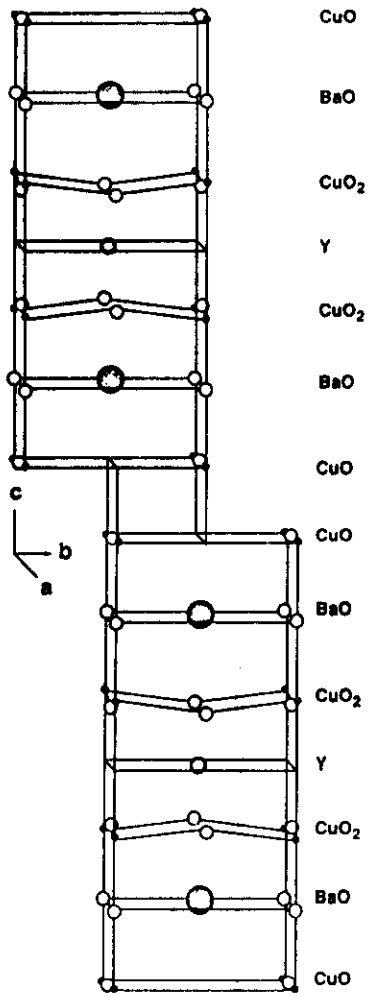
b) distortions (Jahn-Teller) in the CuO_2 plane

→ Composition OK

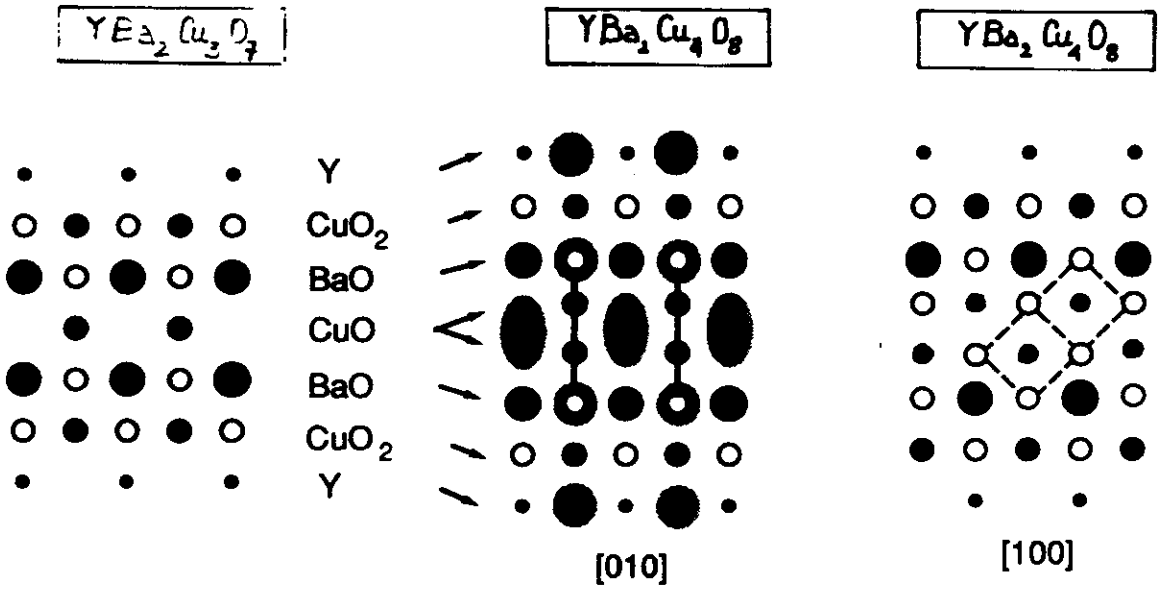
→ Symmetry OK

→ E.D. intensities OK

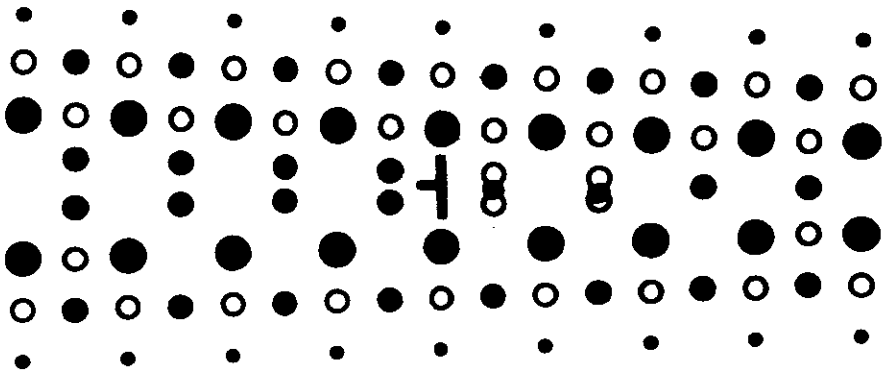

a
b
Oxygen
Copper
CuO_5 Pyramid

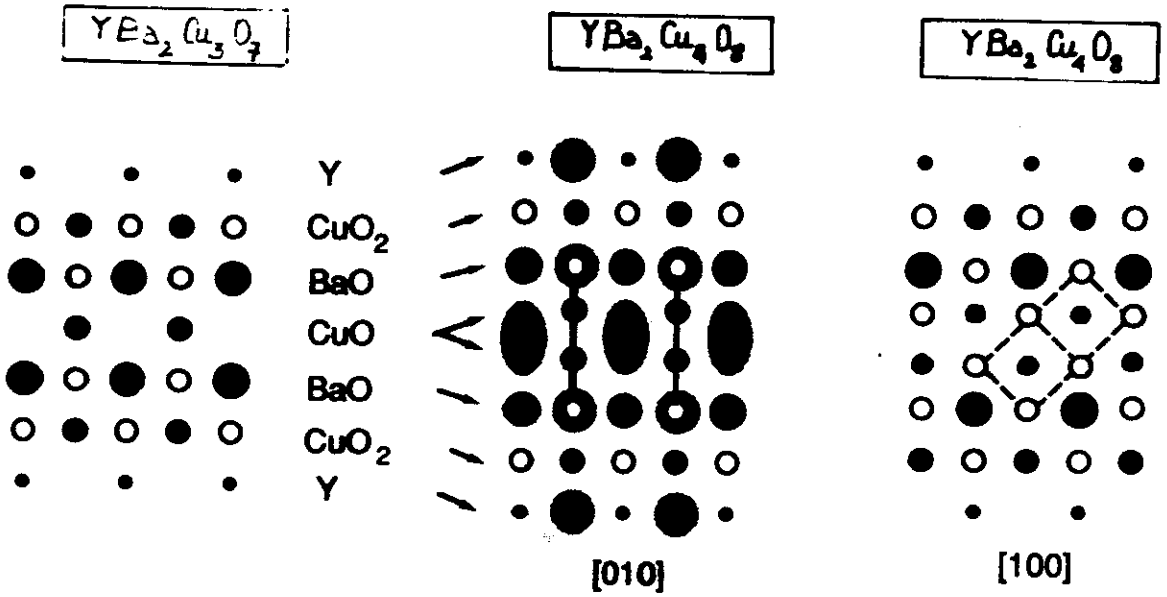

CuO
BaO
CuO_2
Y
CuO_2
BaO
CuO
c
b
a
CuO
BaO
CuO_2
Y
CuO_2
BaO
CuO

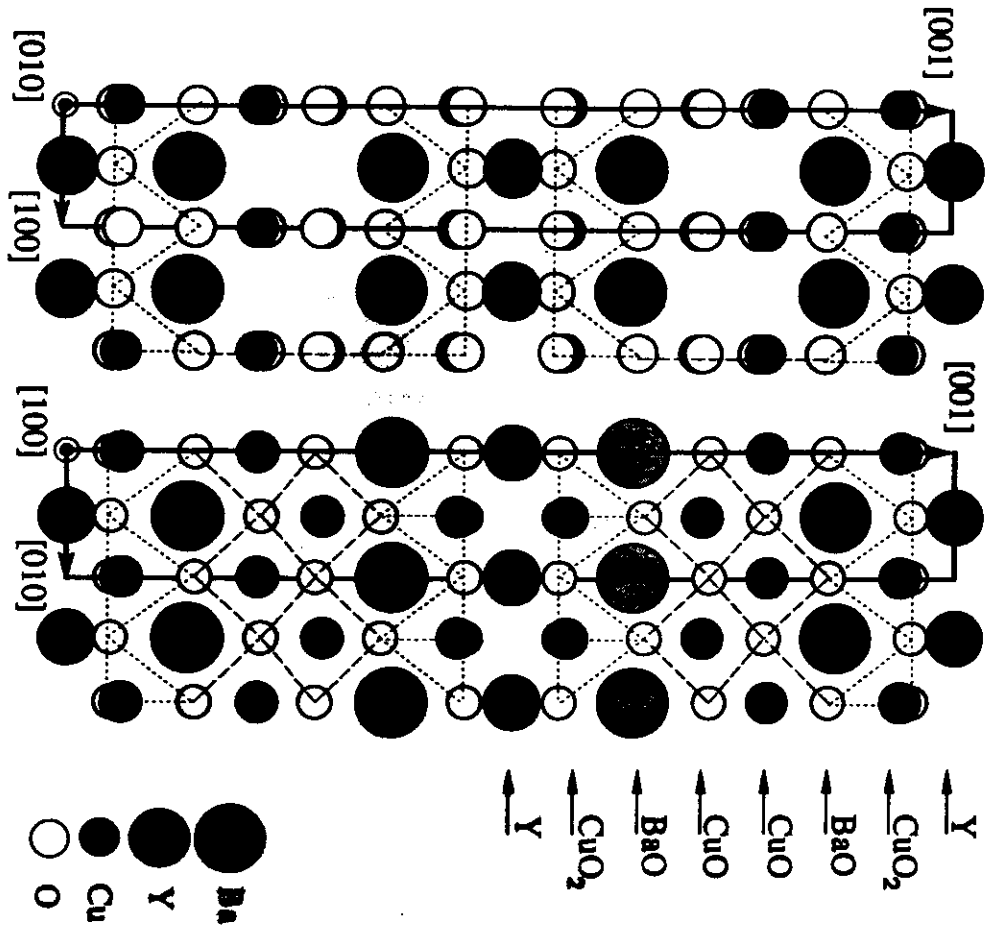
XBL 877-3399



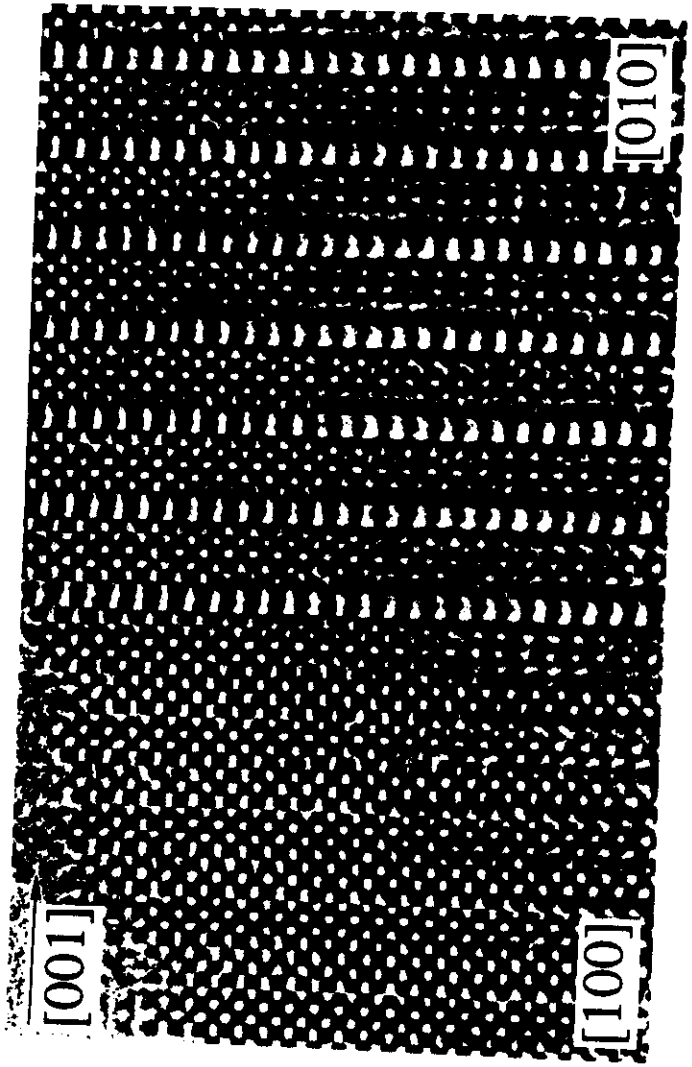
Prismatic Dislocation $\bar{b} = 1/6\, c\,[001]$




YBa2Cu3O7
YBa2Cu4O8
YBa2Cu4O8
Y
CuO2
BaO
CuO
BaO
CuO2
Y
[010]
[100]


[010]
[001]
[001]
[001]
[001]
[010]
Y
CuO2
BaO
CuO
CuO
BaO
CuO2
Y
O
Cu
Y
Ba

YBa2Cu4O8



MODULATED STRUCTURE

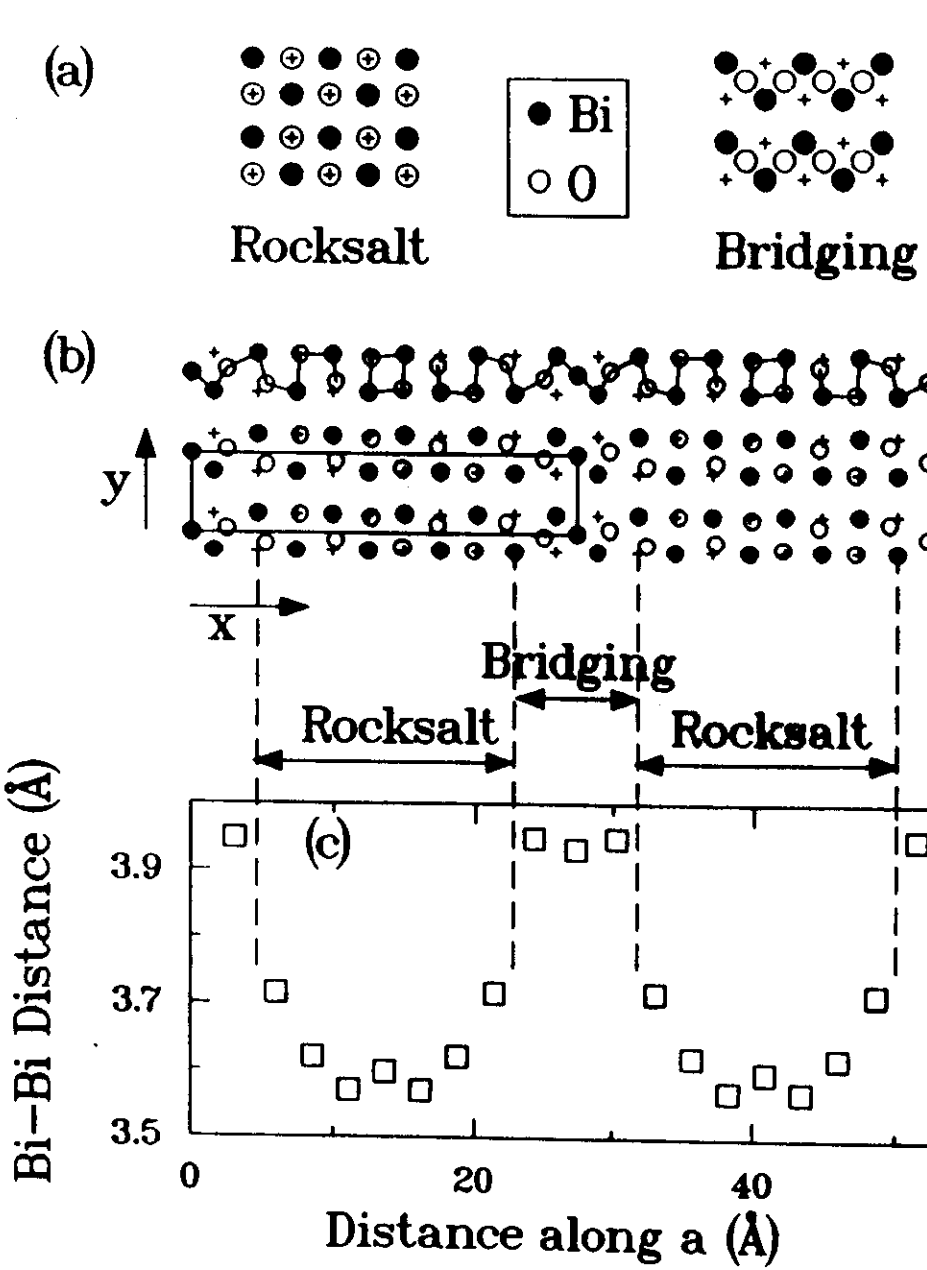
MODELS ??

- EXTRA OXYGEN
- Sr ↔ □
- Bi → Cu
  Sr → Bi
- ....

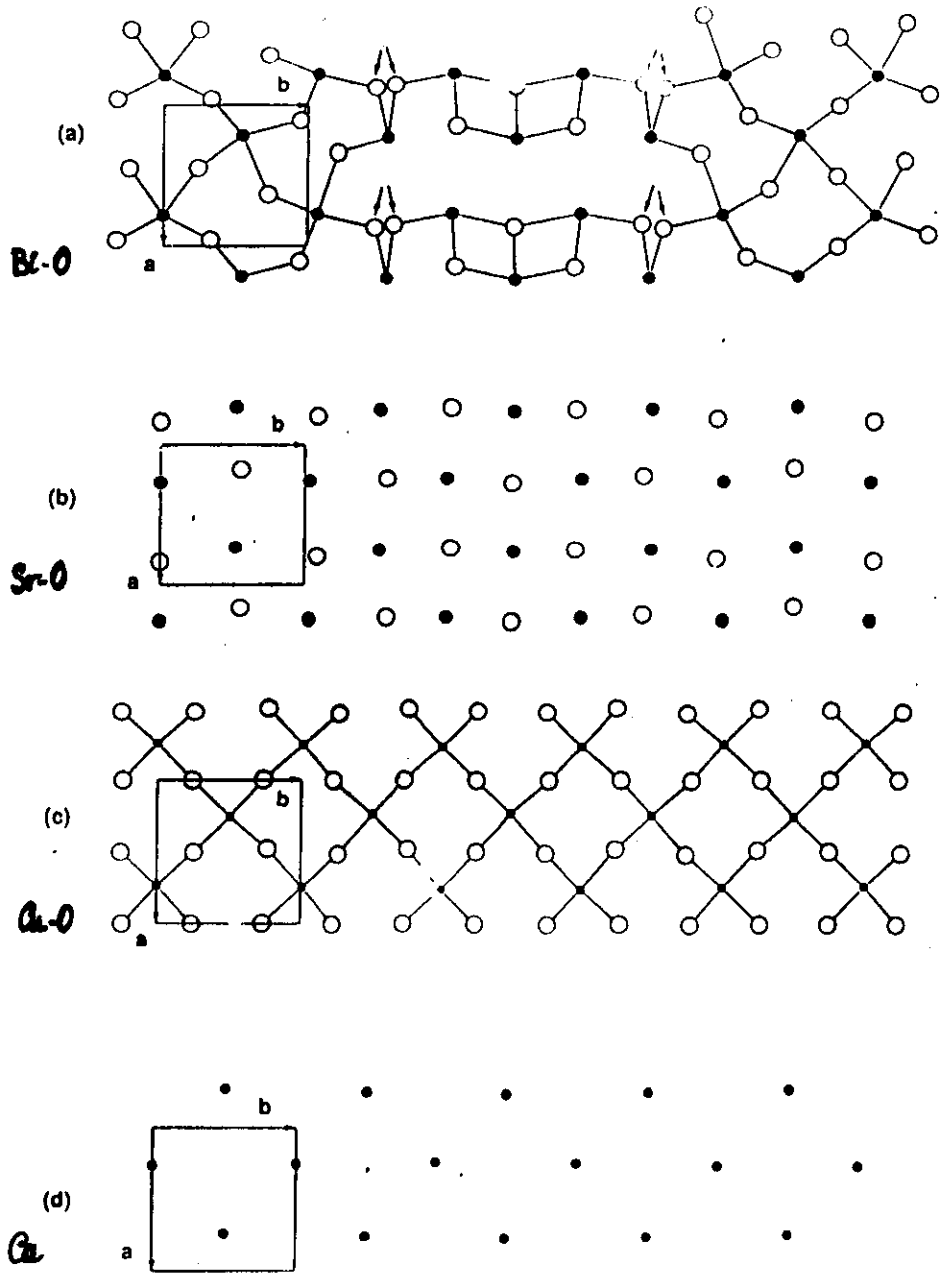
EM DATA

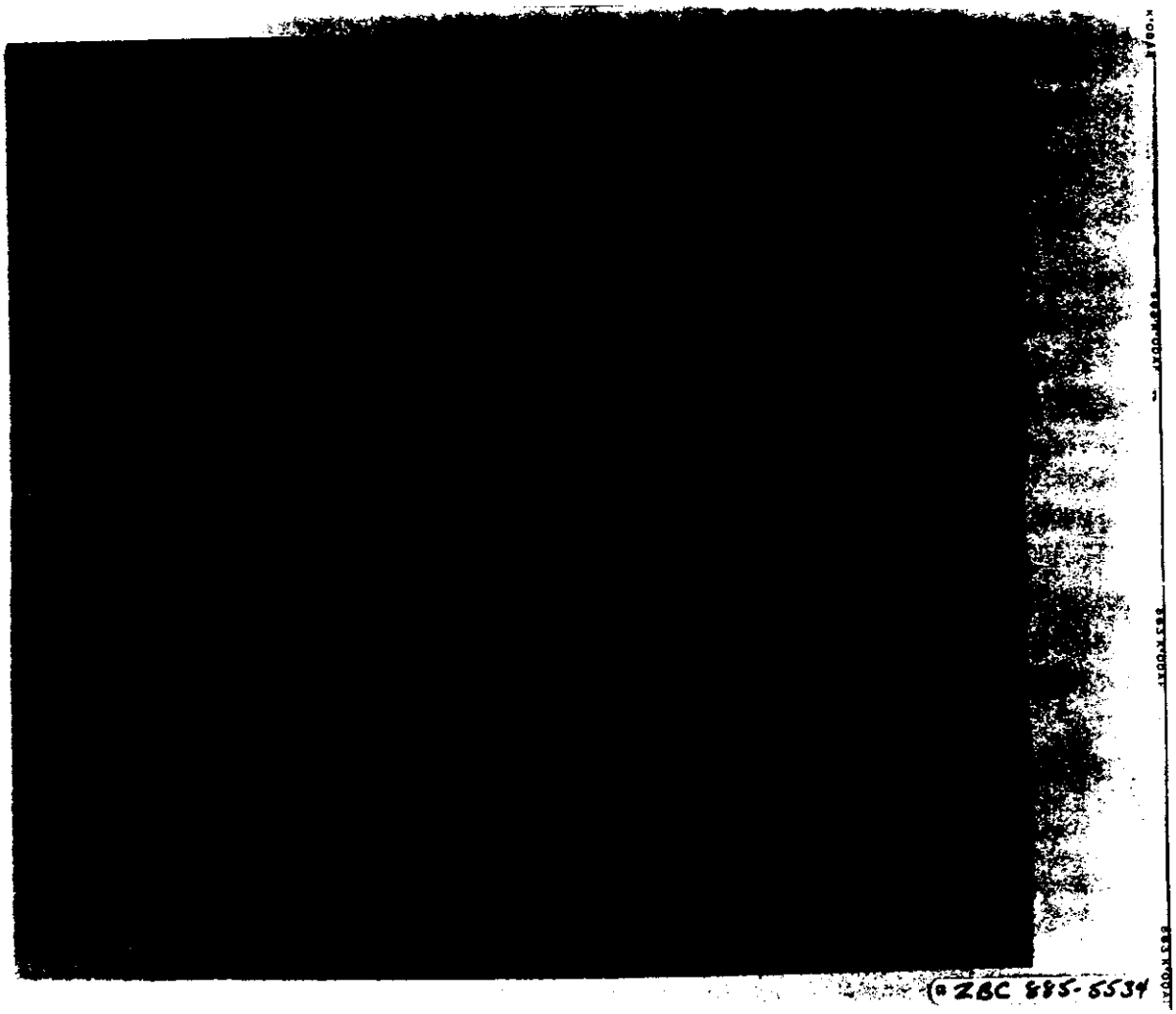
- NO TEMP DEPENDENC
- I(hklm) ↘ with m ↗
- $Sr_2 \rightarrow Sr_{2-x} La_x (Ba_x)$
- MAX. MOD. IN BiO-PLAN.
- e^- IRRAD. → MOD. CHAN

EXTRA OXYGEN → Bi-COORDIN. CHANGE



Le Page et al
→ Phys Rev B





$Bi_2Sr_2Ca_nCu_{1+n}O_{6+2n}$	Short notation	c/2 (nm)	Tc (K)
2 2 0 1 (n=0)	A	1.2	20
2 2 1 2 (n=1)	B	1.53	80
2 2 2 3 (n=2)	C	1.9	110
2 2 3 4 (n=3)	D	2.2	135 ?

REAL SPACE MODULATION

a) reconstruct 3D reciprocal space of the modulated structure

b) deduce the complete Bravais symbol of the 4D structure

c) derive the modulation function (for each atom type) from superspace symmetry

(see De Wolff Acta Cryst 1977 and De Wolff et al. Acta Cryst 1981)

Application to $Bi_2Sr_2Ca_2Cu_3O_{10}$ and $Tl_2Ba_2CuO_6$

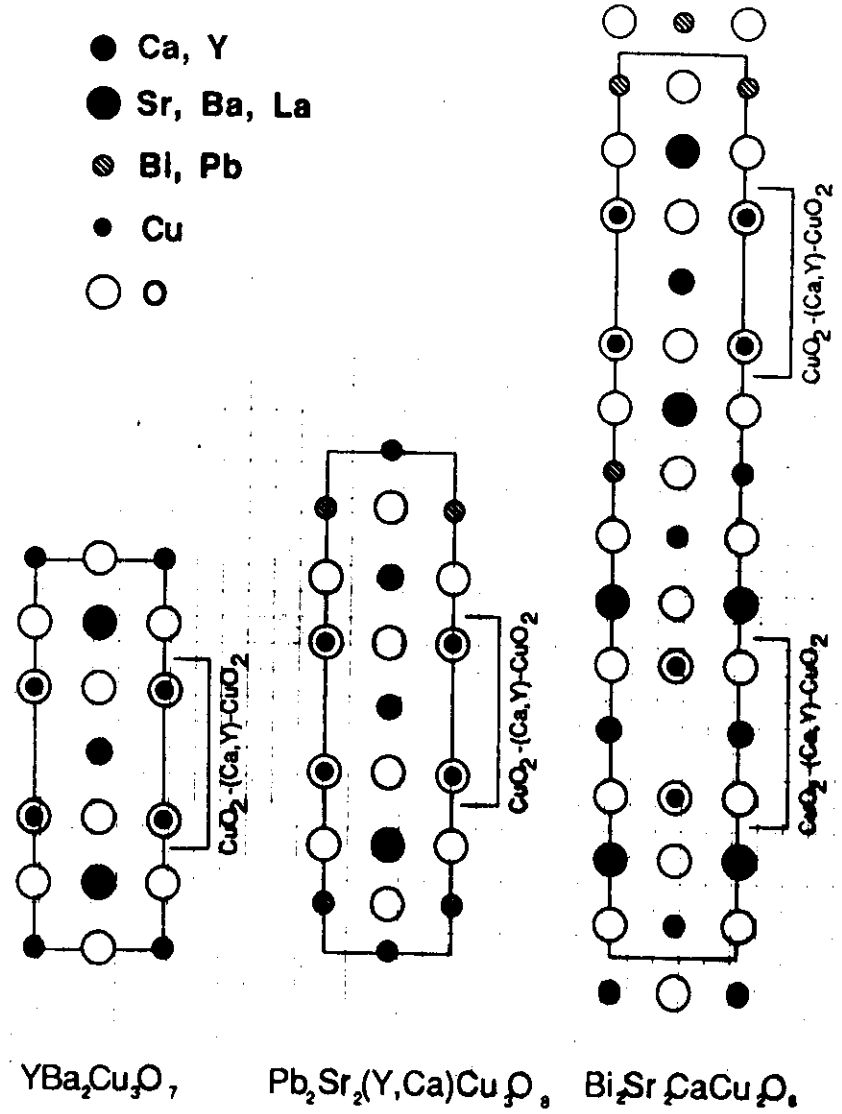


fig 1

ELECTRON MICROSCOPY FOR MATERIALS SCIENCE

Instruments	Purch.	Acc. Voltage	Resolving Power	Applications
JEOL JEM 1250	1973	1250 kV	4 Å	MICROELECTRONIC COMP. IRRADIATION SIMULATION PHASE TRANSITIONS
JEOL JEM 4000 EX	1988	400 kV	1.7 Å	HIGH RESOLUTION E.M. STRUCTURE DETERMINATION DEFECT CHARACTERIZATION
JEOL JEM 200 CX	1980	200 kV	2.5 Å	
JEOL JEM 100 C	1972	100 kV	5 Å	STEM X-RAY MICROANALYSIS SIDE ENTRY CONFIGURATION
PHILIPS EM 300	1967	100 kV	10 Å	PHASE TRANSFORM. STUDIES ELECTRON DIFFRACTION
JEOL JSM T220A	1987	40 kV		SCANNING EL.MIC. SURFACE STUDIES

Y-Ba-Cu-O

A. $YBa_2Cu_3O_{7-\delta}$

- structure des macles (110)
- défauts (001)
- l'influence de l'oxygène
  $O\ l \rightarrow 2a_p \rightarrow (na_p) \rightarrow 2\sqrt{2} \times 2\sqrt{2} \rightarrow$ cubic
- le plateau 60 K à $O_{6.5}$-$O_{6.6}$ (K.U. Leuven)
- la structure $2\sqrt{2} \times 2\sqrt{2}$ (Argonne Nat. Lab.)
- les irradiations aux ions lourds (Orsay)
- substitutions de Cu par Fe (ULB Bruxelles)

B. $YBa_2Cu_4O_8$

(Philips Eindhoven)