INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392-1

SMR/384 - 9

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

HTS CHEMISTRY
(Lecture III)

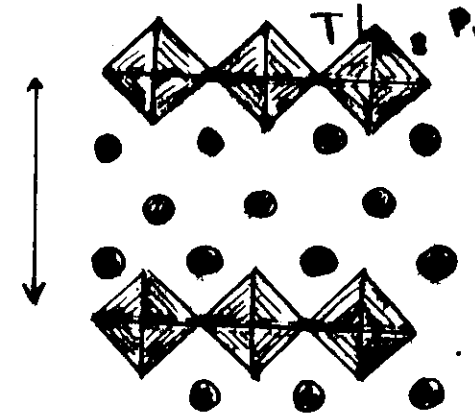
Bernard RAVEAU
Laboratoire Crismat - I.S.M.R.A.
Université de Caen
Boulevard du Marechal-Juin
14032 Caen Cedex
France

[1,2]. Cuprates.

- predicted compositions: $Tl\,Ba_2\,CuO_5$ or $Tl\,Sr_2\,CuO_5$.
- introduction of Pb(IV) or Pr(IV) in order Cu(III) ↘.

⇓

- $Tl_{0.5}\,Pb_{0.5}\,Sr_2\,CuO_5$ Not superc
- $Tl_{1-x}\,Pr_x\,Sr_{2-y}\,Pr_y\,CuO_5$
- $Tl_{0.6}\,Pr_{0.6}\,Sr_{1.6}\,CuO_5$, $T_c \sim 40\,K$



Tl, Pr(IV) or Pb(IV). Sr or Sr, Pr(III)

Tl(Pb)-O : { 2.04 × 2 (Å) ; 2.64 × 4

Tl(Pr)-O : { 2.14 × 2 (Å) ; 2.64 × 4

(2)

$[A\,Cu\,O_{3-x}]_m\,[A\,O]_n$ — CuO_2

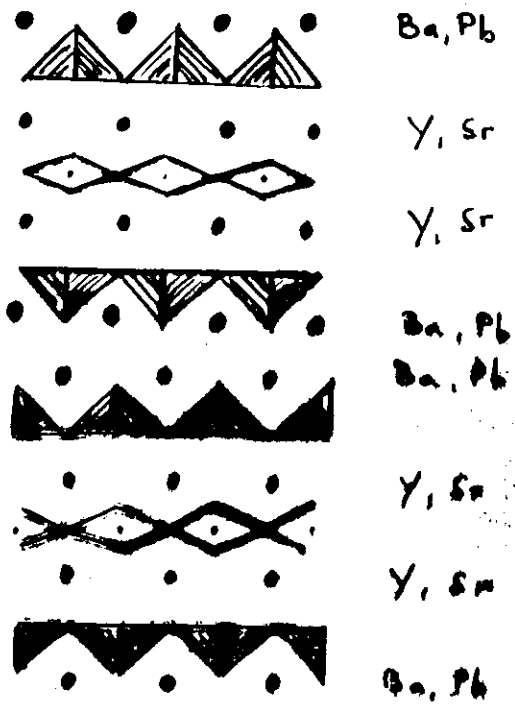
	m = 1	m = 2	m = 3	m = 4
n = 1	[1,1] 0201 $La_{2-x}A_xCuO_4$	[2,1] 0212 $La_{2-x}A_{1+x}Cu_2O_6$	[3,1] 0223 $PbBaSr\,YCu_3O_8$	[4,1] 0234 (...)
n = 2	[1,2] 1201 $Tl_{1+x}A_{2-x}CuO_5$ $Tl_{0.7}Pr_{0.3}Sr_2CuO_5$	[2,2] 1212 $TlBa_2CaCu_2O_7$	[3,2] 1223 $TlBa_2Ca_2Cu_3O_9$	[4,2] 1234 $TlBa_2Ca_3Cu_4O_{11}$
n = 3	[1,3] 2201 $Tl_2Ba_2CuO_6$ $Bi_2Sr_2CuO_6$	[2,3] 2212 $Tl_2Ba_2CaCu_2O_8$ $Bi_2Sr_2CaCu_2O_8$	[3,3] 2223 $Tl_2Ba_2Ca_2Cu_3O_{10}$ $Bi_{2-x}Pb_xSr_2CaCu_2O_8$	[4,3] 2234 $Tl_2Ba_2Ca_3Cu_4O_{12}$

(1)

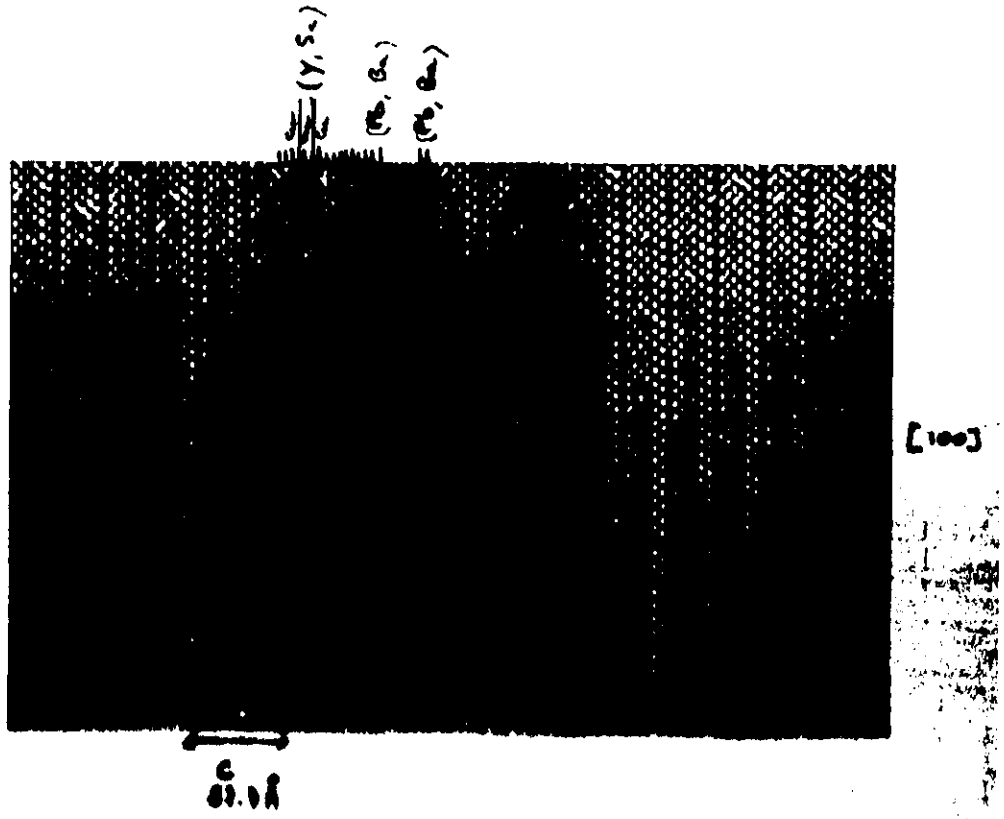
. [3,1] – cuprate .

$PbBaYSrCu_3O_8$ Not superc.

Tet $a = 3.84$ Å $\quad c = 27.66$ Å



© ℓ ℓ 3.



$PbBa(YSr)Cu_2O_8$

Lead Substitution in $Pb_2 Sr_2 Ca Cu_3 O_8$

$$Pb_{2-x} Bi_x Sr_2 Y_{1-y} Ca_y Cu_3 O_8$$

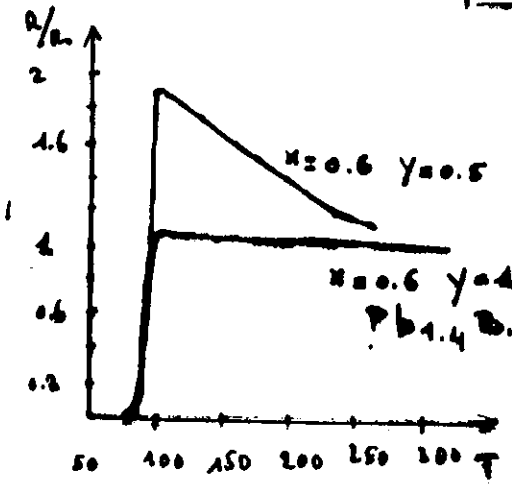
$$\Downarrow$$

- New Superconductors $\quad 0 \leqslant x = y \leqslant 0.60$

  $x = 0.60 \quad y = 0.5$

  $x = 0.60 \quad y = 1.$

- Bi (III) ⟶ P (I).
- Tc ↑ ⟶ zero resistance at $\boxed{T_c \approx 99\,K.}$

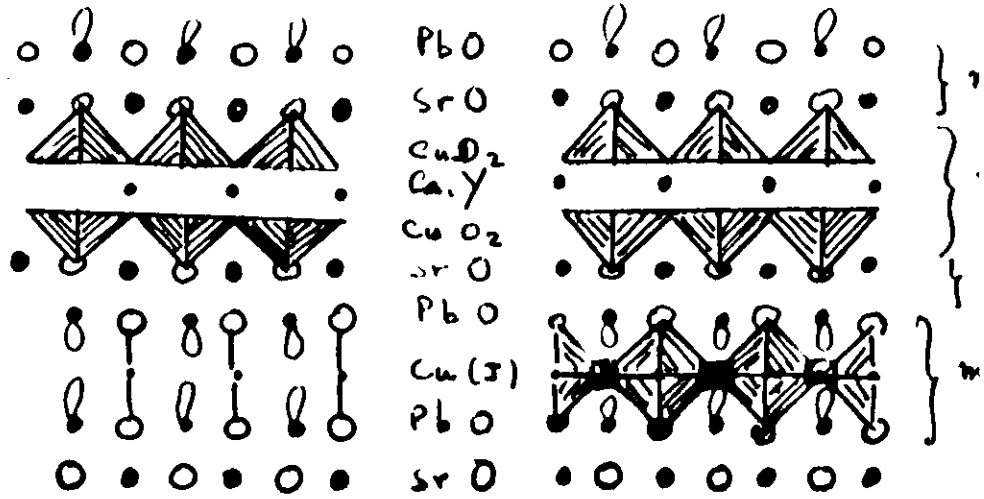


to be compared to $T_c \approx 46K$ (Rao) without lead.

T_c onset ≈ 100K.

(E)

What about $Pb_2 Sr_2 Y_{1-x} Ca_x Cu_3 O$



$Pb_2 Sr_2 Y Cu_3 O_8$ "$Pb_2 Sr_2 Y Cu_3 O_{10}$

Cava's Description: Double intergrow

PbO layers in of [2,1] and

"$Y Ba_2 Cu_3 O_6$"-type [1,1]

$$\Downarrow$$

$Pb_2 Sr_2 Y Cu_3 O_8 \equiv$ DOUBLE INTERGRO

$$[1,1 / 2,1]$$

S. Perovs. S. R.S Double S. R.S.

Extra Spots in E.D. Patterns: Satellites.

Extra spots and especially <u>satellites</u> are observed for many cuprates:
ORIGIN of SATELLITES ? RELATION WITH SUPERCONDUCTIVITY ?

Ln.-alkaline earth Cuprates: No satellites

Thallium cuprates: very rarely observed, and only by some authors.

Bismuth cuprates: Always observed and SPECTACULAR !

Lead cuprates: ?

IS THE PARTICULAR BEHAVIOR OF Bi-CUPRATES RELATED TO THE $6s^2$ Lone pair of Bi(III). ?

BISMUTH CUPRATES

origin: use $6s^2$ lone pair cation, Bi(III) (Berkeley. June 87).

- Lamellar morphology -

a) cleavage of the crystals between the layers

b) long distance between the "Bi"-Layers. 3.2 Å !

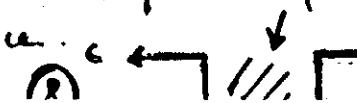
} stereoactivity of the lone pair.

- satellites in incommensurate positions.

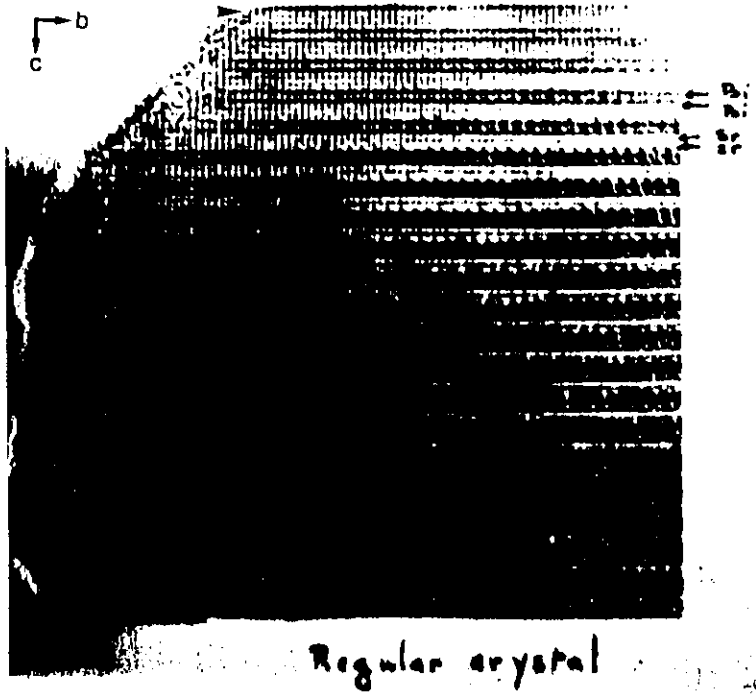
q ranging from 4.7 to 5.

a) along one direction [100] or [010]

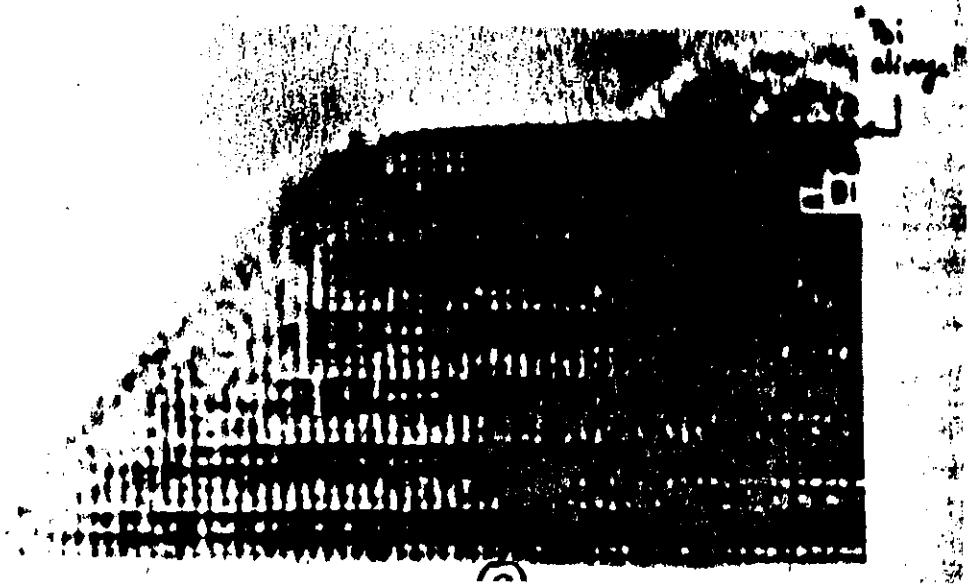
b) along two perpendicular directions
- superimposed crystals
- domains at 90° in the same crystal: perfect coherent interface.



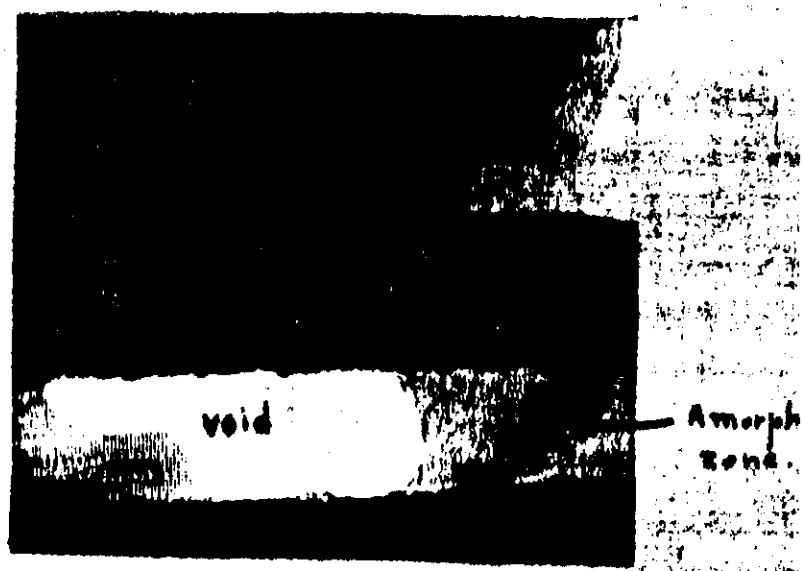
2201
$Bi_2Sr_2CuO_6$



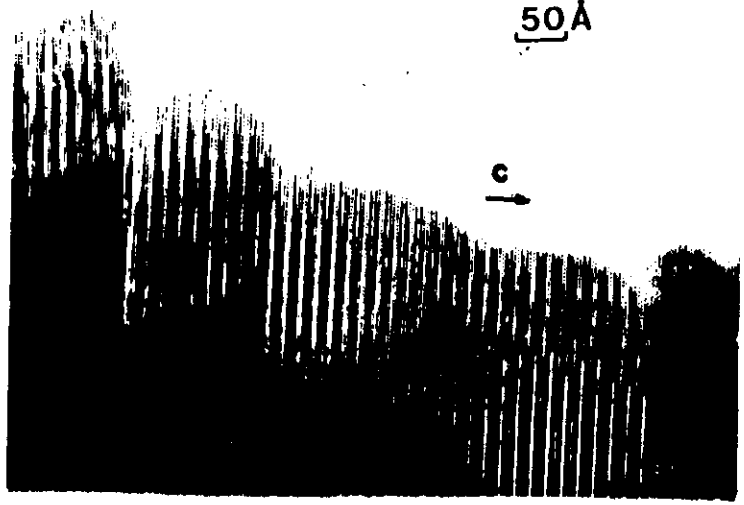
Regular crystal

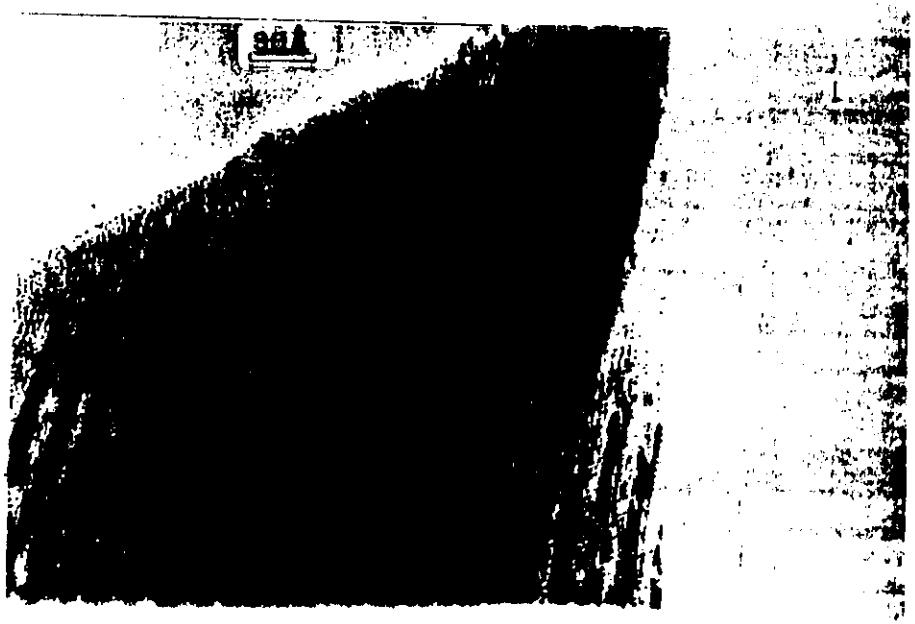


- $Bi_2Sr_2CaCu_2O_8$ -



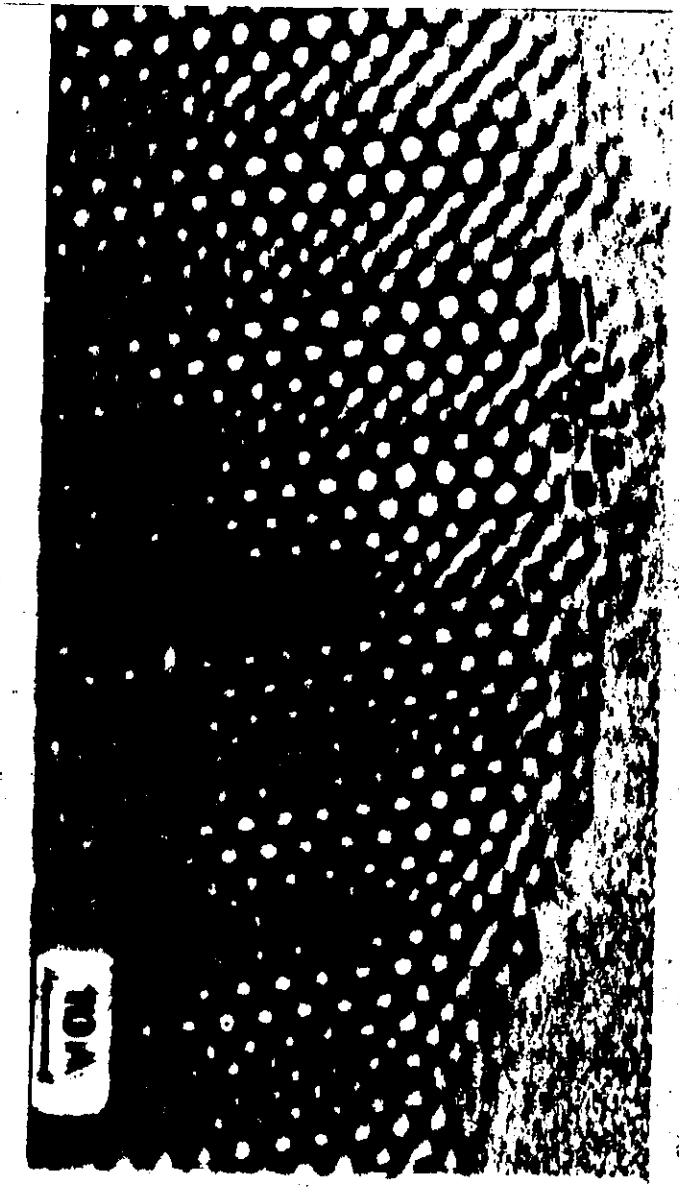
[001]





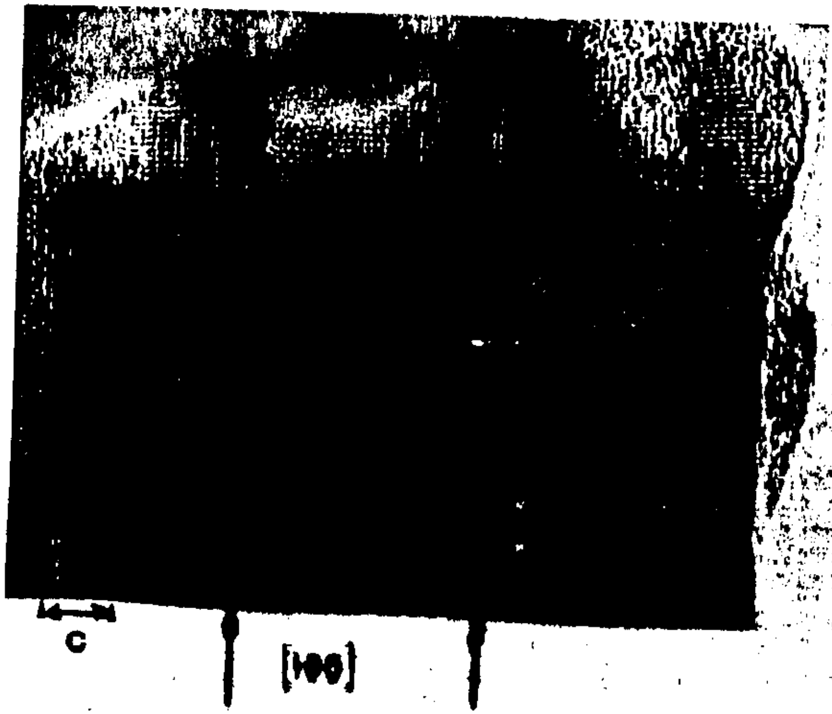
(11)

$Bi_2Sr_2CaCu_2O_8$

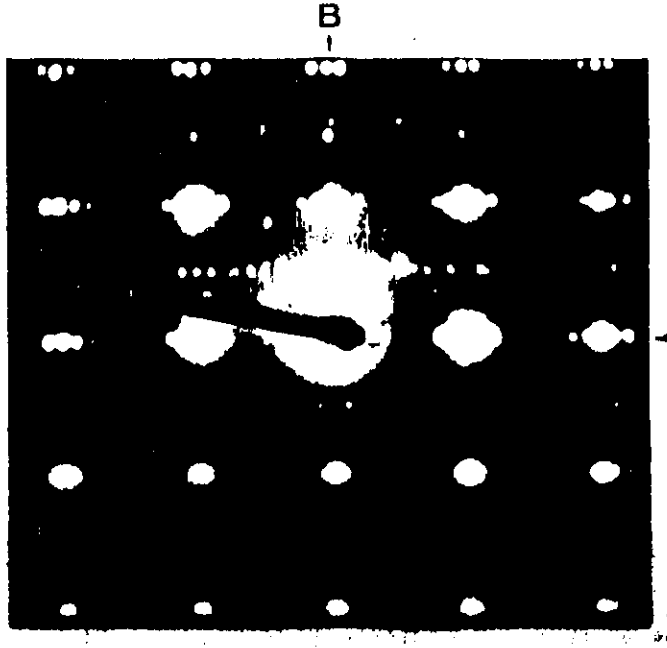


(12)

$Bi_2Sr_2CaCu_2O_8$: defects



"24.5 Å" members



A satelli... in incommen-rable pos...

$Bi_2Sr_2CaCu_2O_8$: INCOMMENSURABILITY

Satellites ... perpendicular directions in a superposed lamella

Rôle of the Lone pair in incommensurability.

- Substitution of Cu by Fe in Bi-cuprates.
- Substitution of Bi by Pb in $Bi_2Sr_2CaCu_2O_8$.
- E. D. study of lead cuprates:
  - $(Pb_{...})(Y\ Sr)\ Cu_3O_8$
  - $Pb_2Sr_2\left(\begin{smallmatrix}Ca\\Y\end{smallmatrix}\right)Cu_3O_8$
  - $Pb_{2-x}Bi_xSr_2\left(\begin{smallmatrix}Ca\\Y\end{smallmatrix}\right)Cu_3O_8$
- $Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_8$.

Remark: Pb(II), Bi(III) and Tl(I) are characterized by 6s² L.P.
Not Tl(III).

origin of the satellites and relations with superconductivity.

[•] Cu ⟶ Fe.

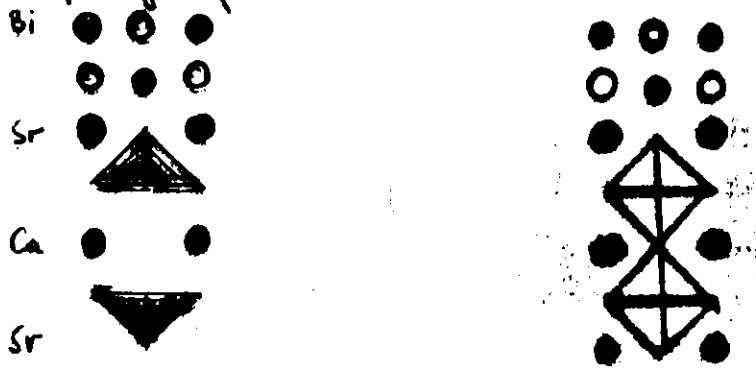
$Bi_2 Sr_{3-x} Ca_x Fe_2O_9$ isostruct. $Bi_2 Sr_2 Ca Cu_2 O_8$

$Bi_2 Sr_4 Fe_2 O_{12}$ isostruct. $Bi_2 Sr_2 Ca_2 Cu_3 O_{10}$

CuO_5 pyramids

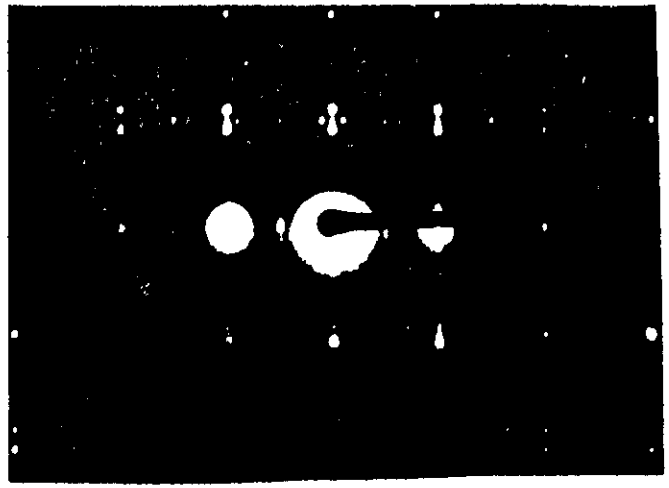
CuO_4 groups

CuO_6 octah.



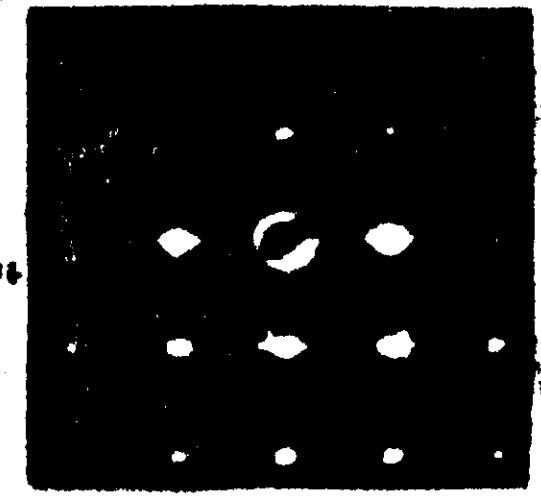
- Lamellar crystals
- Similar satellites on E.D. patterns
- similar modulations on H.R. [010] H.R.E.M. images

$Bi_2 Sr_3 Fe_2 O_9$



[001]

$Bi_2 Sr_4 Fe_2 O_{12}$



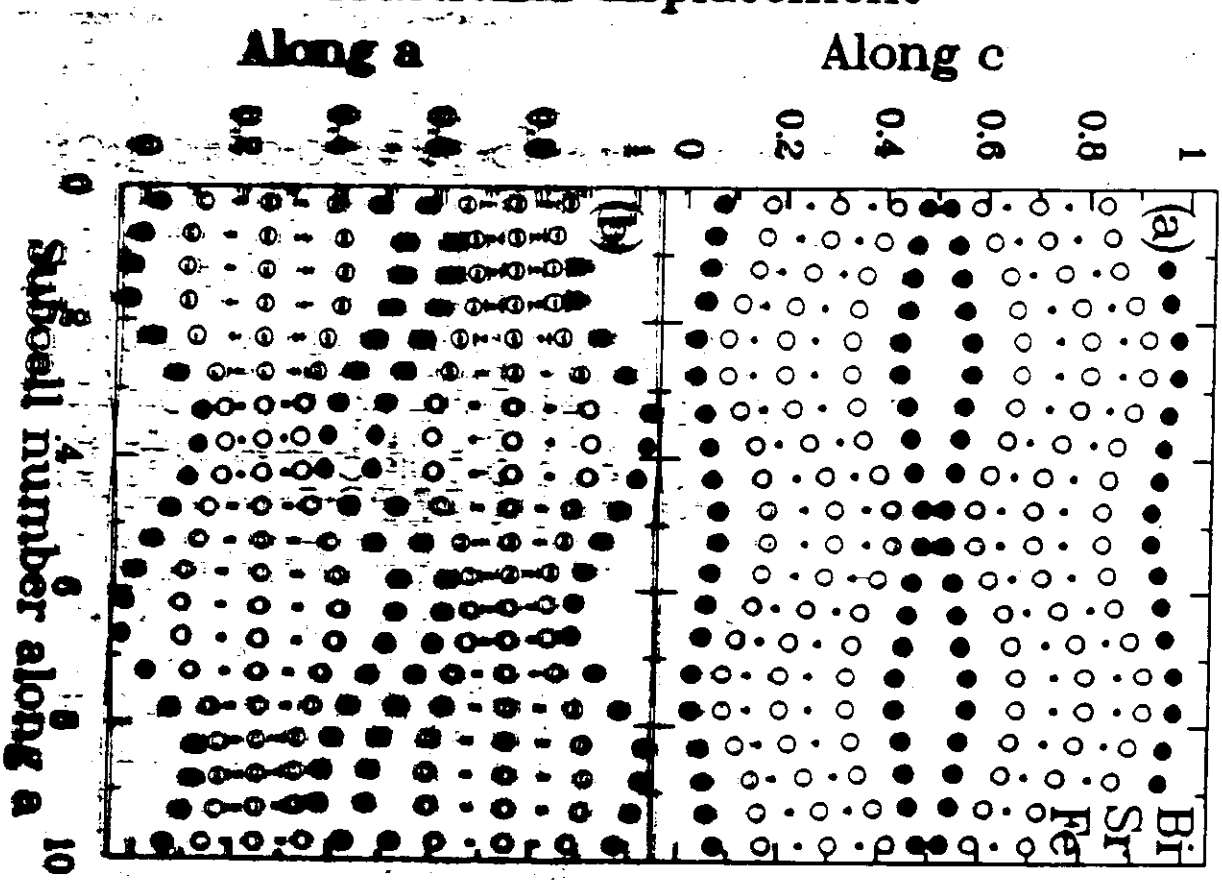
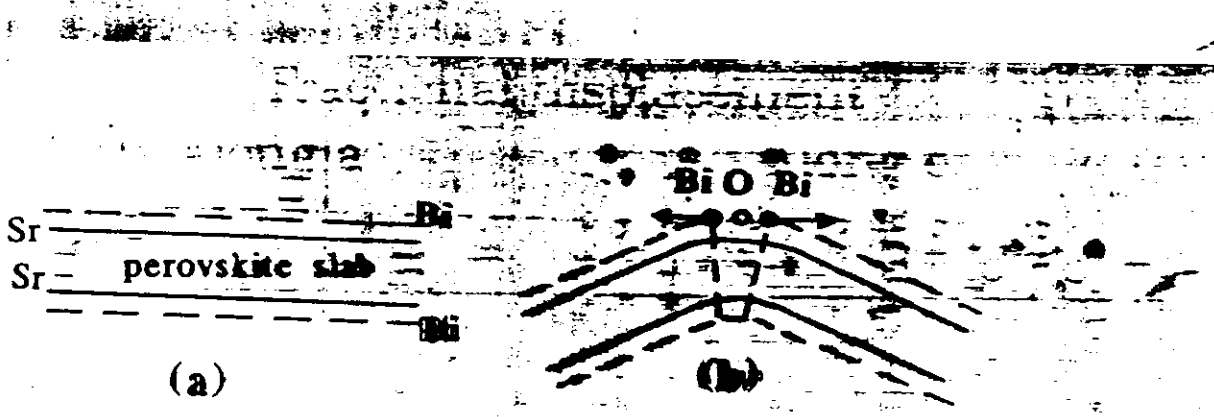
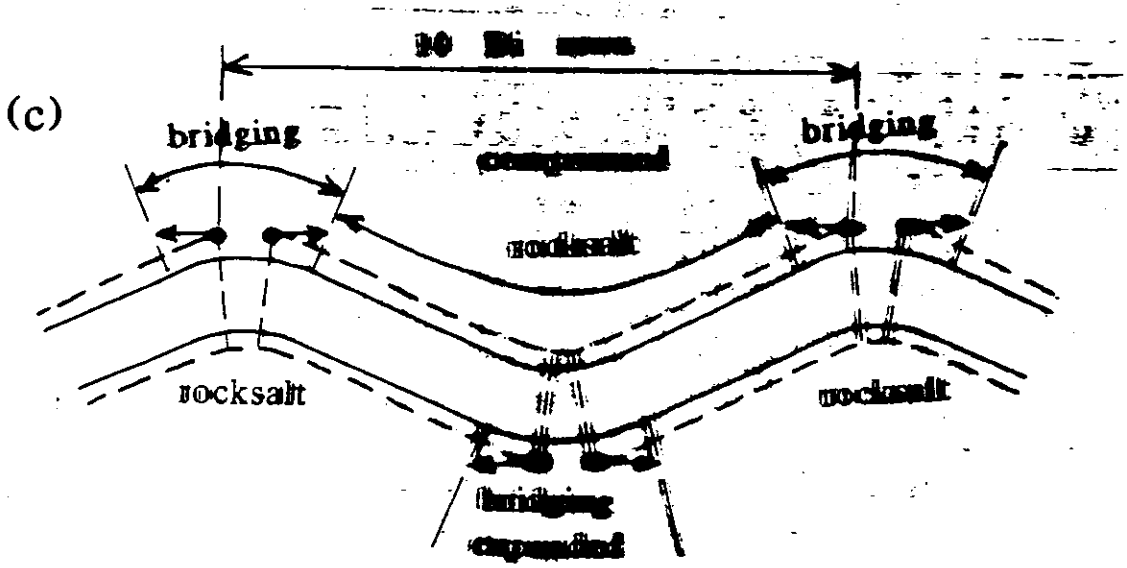

Fractional displacement
Along a
Along c
0
0.2
0.4
0.6
0.8
1
Subcell number along a
0
2
4
6
8
10
(a)
(b)
Bi
Sr
Fe

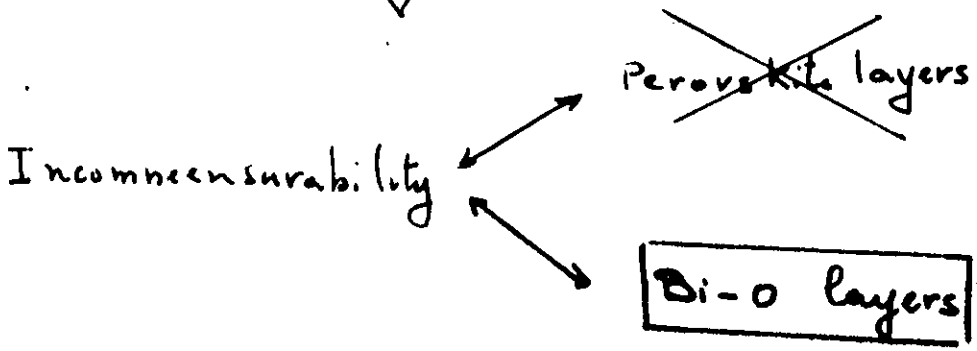
Fig. 2


Bi O Bi
Sr
Bi
Sr
perovskite slab
Bi
(a)
(b)


(c)
bridging
bridging
rocksalt
rocksalt
rocksalt

- Simultaneously structure of one Bi-Fe phase (TARASCONetal) → Waving of bismuth layers.

⇓



⇓

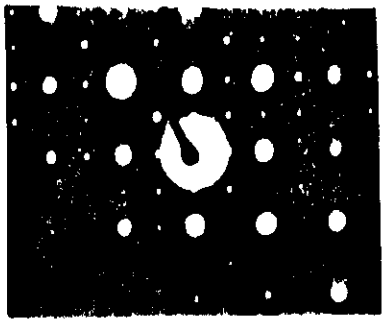
Hypothesis: STEREOACTIVITY of the $6s^2$ Bi(III) lonepair → distortion of the rock salt layers → i.e. a non-periodic displacement of Bi(III) and Oxygen atoms.

⊡ $(Bi_{2-x}Pb_x)Sr_2(Ca_{1-x}Y_x)Cu_2O_8$

- "2212"-structure : $0 \leq x \leq 1$
- Superconducting for $x < 0.5$: $T_c = 80K$ ($R=0$). $BiPbSr_2YCu_2O_8$ does not superconduct ($x=1$).
- Space Group has changed with respect to $Bi_2Sr_2CaCu_2O_8$: Pnma instead of Amaa.
- Classical modulations of Bi-cuprates have disappeared but are replaced by new types of satellites.

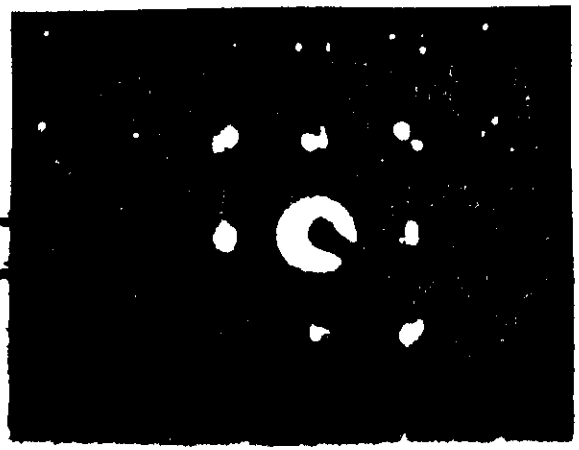
⇓

Modulations are due to the $6s^2$ lonepair of Bi(III) as well as Pb(II).

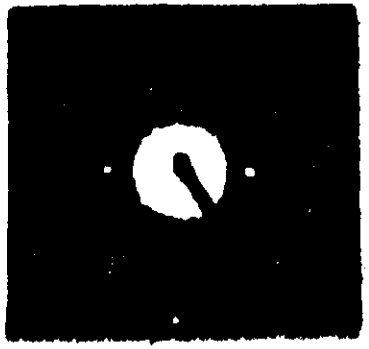


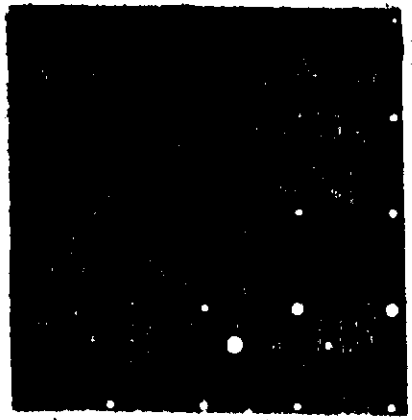
(001)

Two Misoriented Lattices + D. $\vec{q}$.



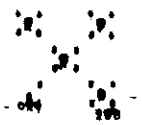
Zones désorientées





Periodicity $\approx 6\,d$

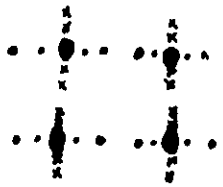
satellites along $[210]^*$



$BiPbSr_2YCu_2O_8$

$\boxdot$ $PbBa(SrY)Cu_3O_8$. [3,1]

- All the E. D. Patterns ⟶ satellites



Superposition of two sets of satellites oriented at 90° and DD phenomena.

× • : first order ⅓ d_{110} sat.
× • : " ⅔ d_{110} sat.

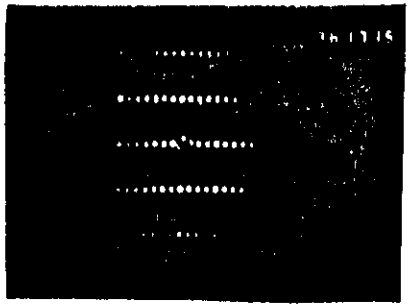
⇓

stereoactivity of Pb(II) as well as Bi(III)

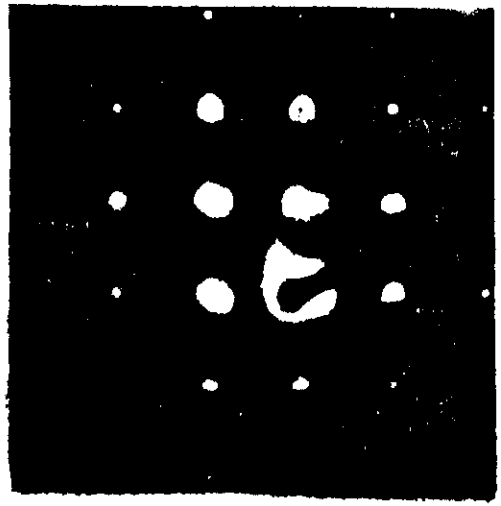
⟹ Distortion of the Rocksalt layers

⟹ at origin of Incommensurability

[110]



[001]

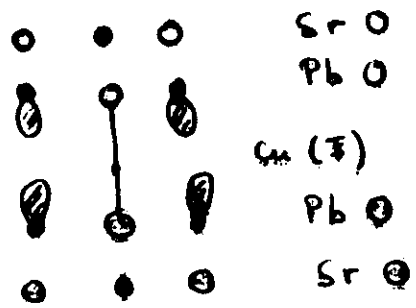


(c)

□ { $Pb_2 Sr_2 Ca_{0.5} Y_{0.5} Cu_3 O_8$ (Cava)
{ $Pb_{2-x} Bi_x Sr_2 \binom{Ca}{Y} Cu_3 O_8$.

⇓

Do not exhibit satellites,
No modulation in spite of
the presence of Bi (III) or Pb (II)



Explanation : The L.P. are directed toward the oxygen vacancies and thus do not disturb the R. S. layer → No distorsion → No modulation.

Incommensurability in

Tl Cuprates

$Tl\,Ba_2\,Ca_{m-1}\,Cu_m\,O_{2m+3}$

$Tl_2\,Ba_2\,Ca_{m-1}\,Cu_m\,O_{2m+4}$

} No satellites.

↓

No $6s^2$ lone pair ⟷ Tl (III)

—

What about Tl (I) ?

($6s^2$ lone pair).

—

⊡ { $Tl\,Sr_2\,Ca\,Cu_2O_7$

{ $Tl_{0.5}\,Pb_{0.5}\,Sr_2\,CaCu_2O_7$

- No satellite for $Tl_2Sr_2CaCu_2O_7$ in agreement with the fact that Tl (III) is not a L.P. cation
- Diffused streaks, Misoriented domains, and some very different satellites in $Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_7$.

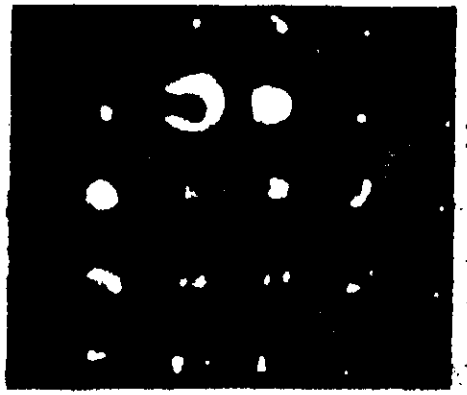
⇓

This suggests that we don't have Pb (II) but Pb (IV) in agreement with Subramanian's result. Here the modulations result from the accommodation of Pb (IV) and Tl (III) in the R.S. layer.

(100) normal

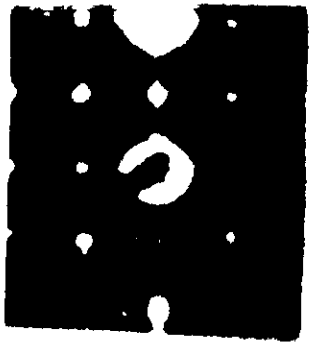
traînées diffusion

(001)



Domaines

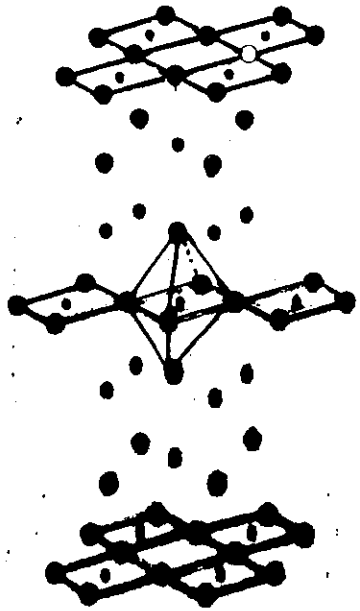
Désorientés



autres satellites suivant [100]

$Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_7$

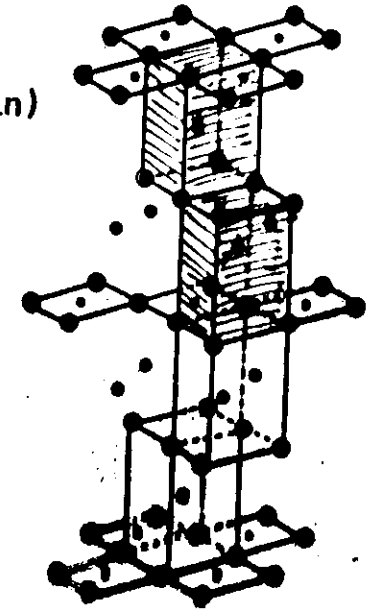
(5a)



• Cu

• Nd(Ln)

• Ox



I

a

La_2CuO_4

b

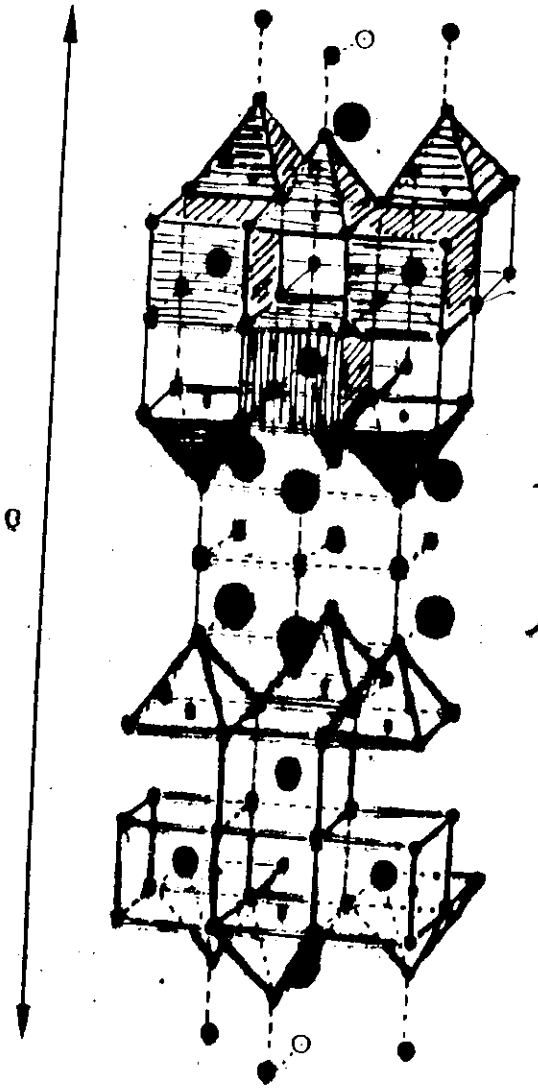
Nd_2CuO_4

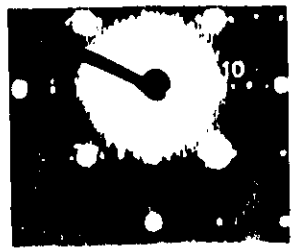
cf fig 7

(30)

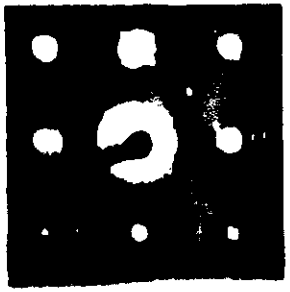
$Tl_{1+x}A_{2-y}Ln_2Cu_2O_9$

- Ln = Pr, Ce
- A = Sr, Ba
- $x \sim 0.3$
- $y \sim 0.3-0.4$

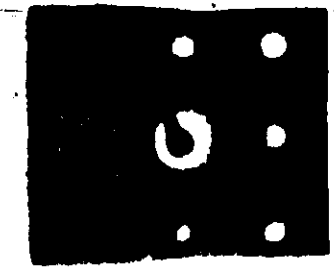




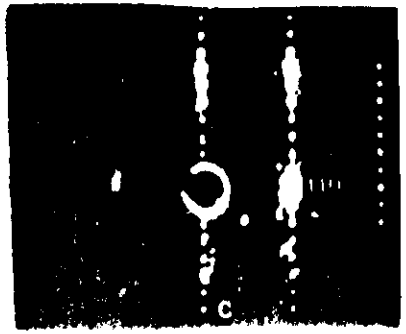
satellites along $\langle 110 \rangle^*$



satellites along $\langle 100 \rangle^*$

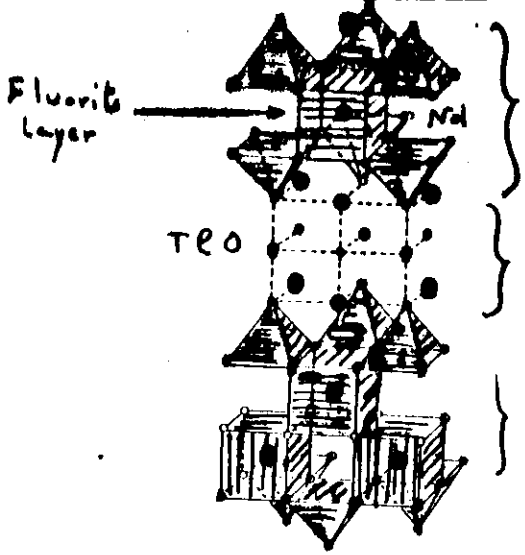


satellites along $\langle 100 \rangle^*$ and $\langle 010 \rangle^*$



complex superimposition of satellites.

$Tl_{1+x}A_{2-y}Ln_2Cu_2O_9$
[001] E.D. patterns.



D.P.
Double Perovskite

Rock Salt Layer

D.F.
Double Fluorite Layer.