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

(11 February - 1 March 1991)

" Structural Aspects of Bi and Tl- Based HTS "

presented by:

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

Structure–properties relationships in high T_c superconductors

- High T_c superconductors are complex oxides with perovskite–type or perovskite–related crystal structures characterized by the presence of CuO_2 layers.

- Superconductivity arises when extra electrons or holes are introduced into the CuO_2 planes by cationic substitutions or oxygen non–stoichiometry.

- The crystal structure of high T_c superconductor can be regarded as built by intercalation of CuO_2 layers and structural blocks which act as "charge reservoir".

- The perovskite–type structure represents the ideal structure for such phenomena since it is very tolerating with respect to cationic size and valence and to oxygen deficency.

- A chemical control of superconductivity exists which drives the transition between magnetismus (AF) and superconductivity.

- This mechanism is not well understood for all the high T_c superconductors.

PEROVSKITE–TYPE STRUCTURE

$$ABO_3$$

$A^{II}B^{IV}O_3$	$CaTiO_3$ $SrTiO_3$ $BaTiO_3$ ....
$A^{III}B^{III}O_3$	$BiFeO_3$ ....
....	....

The perovskite–type structure tolerates oxygen defect so that defective ternary and quaternary oxides can be obtained.

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The "multi-layered" Tl–Ba–Ca–Cu–O (**TBCCO**) and Bi–Sr–Ca–Cu–O (**BSCCO**) high T_c superconductors:

$Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2}$ m=1, 2 n=1, 2, 3, (4, 5)

$TlBa_2CuO_5$		1201
$TlBa_2CaCu_2O_7$	m=1	1212
$TlBa_2Ca_2Cu_3O_9$		1223
$Tl_2Ba_2CuO_6$		2201
$Tl_2Ba_2CaCu_2O_8$	m=2	2212
$Tl_2Ba_2Ca_2Cu_3O_{10}$		2223

$Bi_mSr_2Ca_{n-1}Cu_nO_{2n+m+2}$ m=2 n=1, 2, 3, (4, 5)

$Bi_2Sr_2CuO_6$
$Bi_2Sr_2CaCu_2O_8$
$Bi_2Sr_2Ca_2Cu_3O_{10}$

$(Tl,Pb)_mSr_2Ca_{n-1}Cu_nO_{2n+m+2}$ m=1 n=2, 3

$Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_7$
$Tl_{0.5}Pb_{0.5}Sr_2Ca_2Cu_3O_9$

$(Bi,Pb)_mSr_2Ca_{n-1}Cu_nO_{2n+m+2}$ m=2 n=1, 2, 3

$Bi_{2-x}Pb_xSr_2CuO_6$	**(BPSCCO)**
$Bi_{2-x}Pb_xSr_2CaCu_2O_8$	$x \approx 0.3$
$Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10}$	

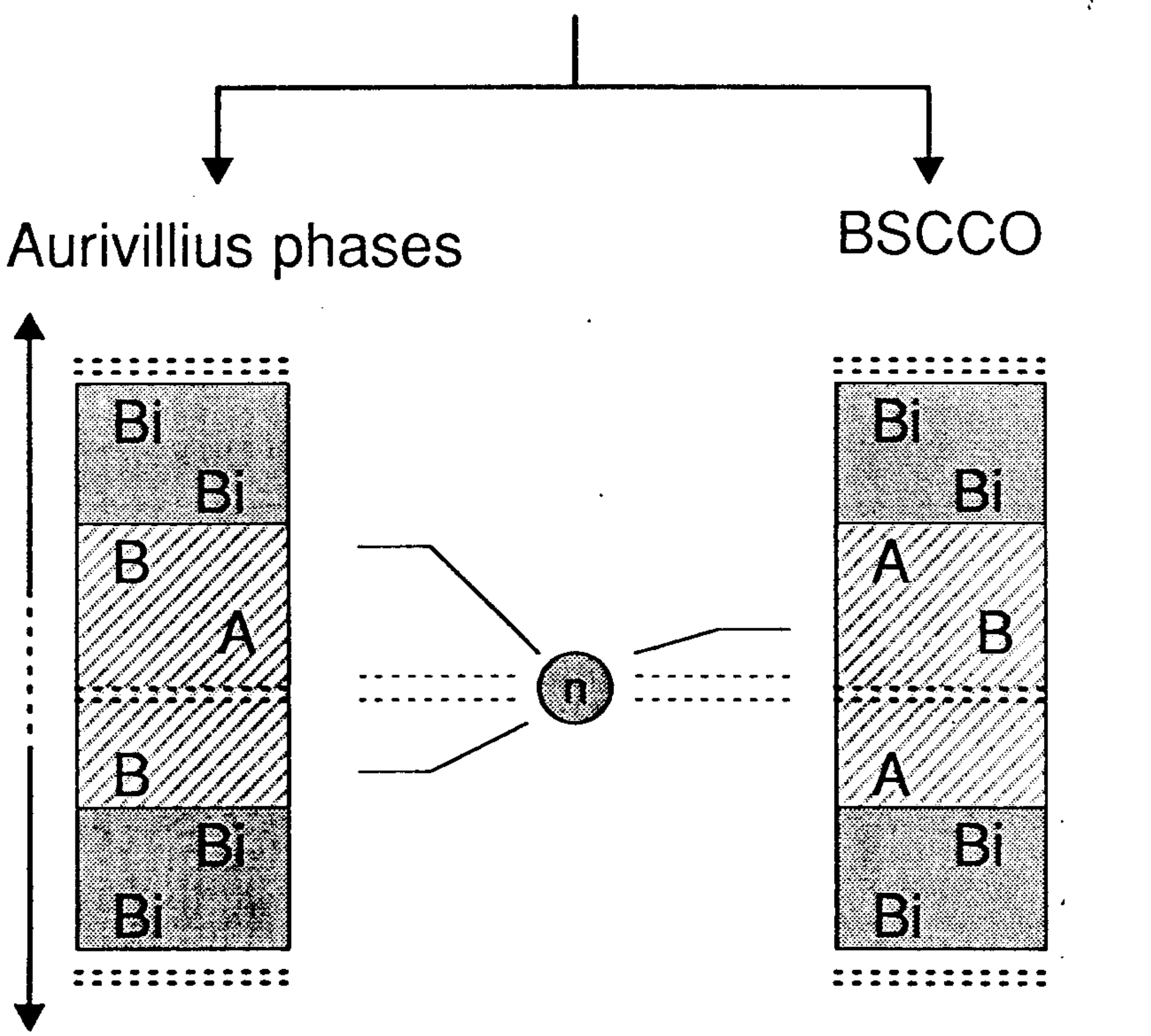
Structural feature

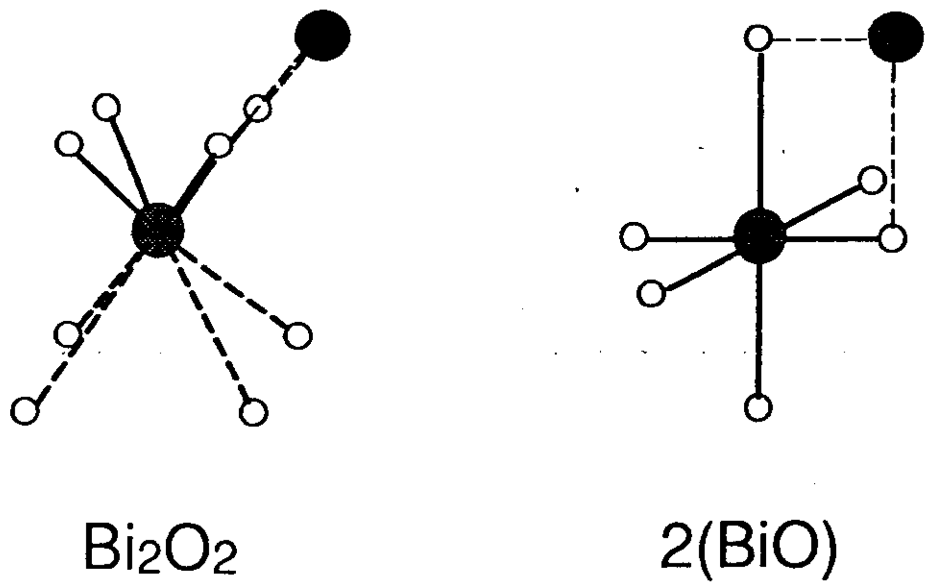
intercalation of two different structural blocks:

– $(TlO)_m$ or $(BiO)_2$ *rocksalt* .

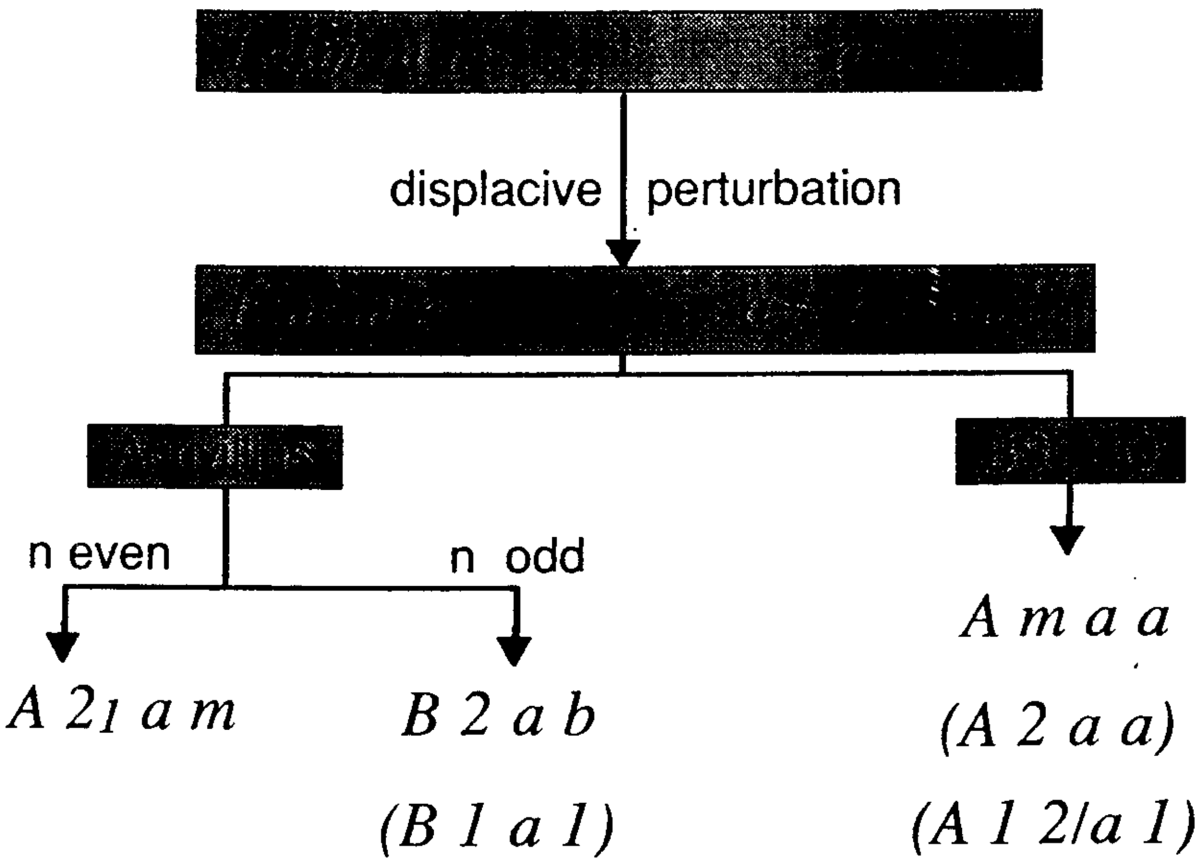
– oxygen deficient Cu containing *perovskite*

Bi_2O_2 ABO_3

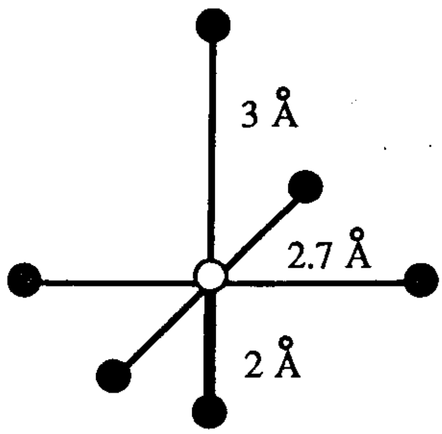




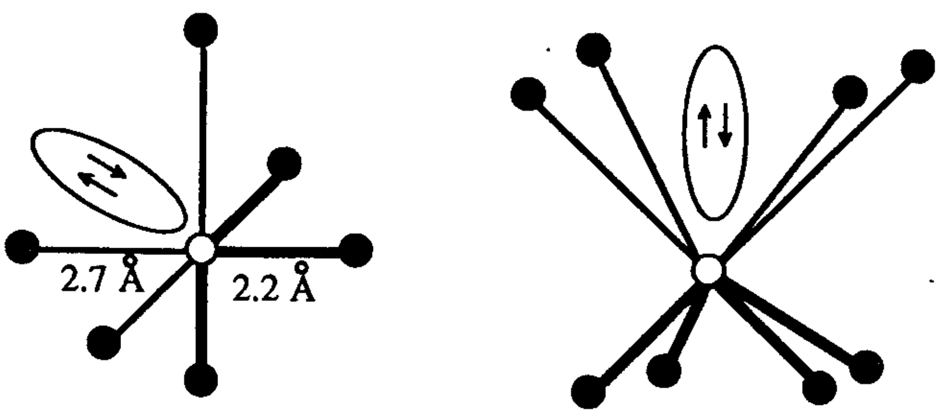
idealized structure



Bi coordination in the unmodulated structure



Typical Bi coordinations



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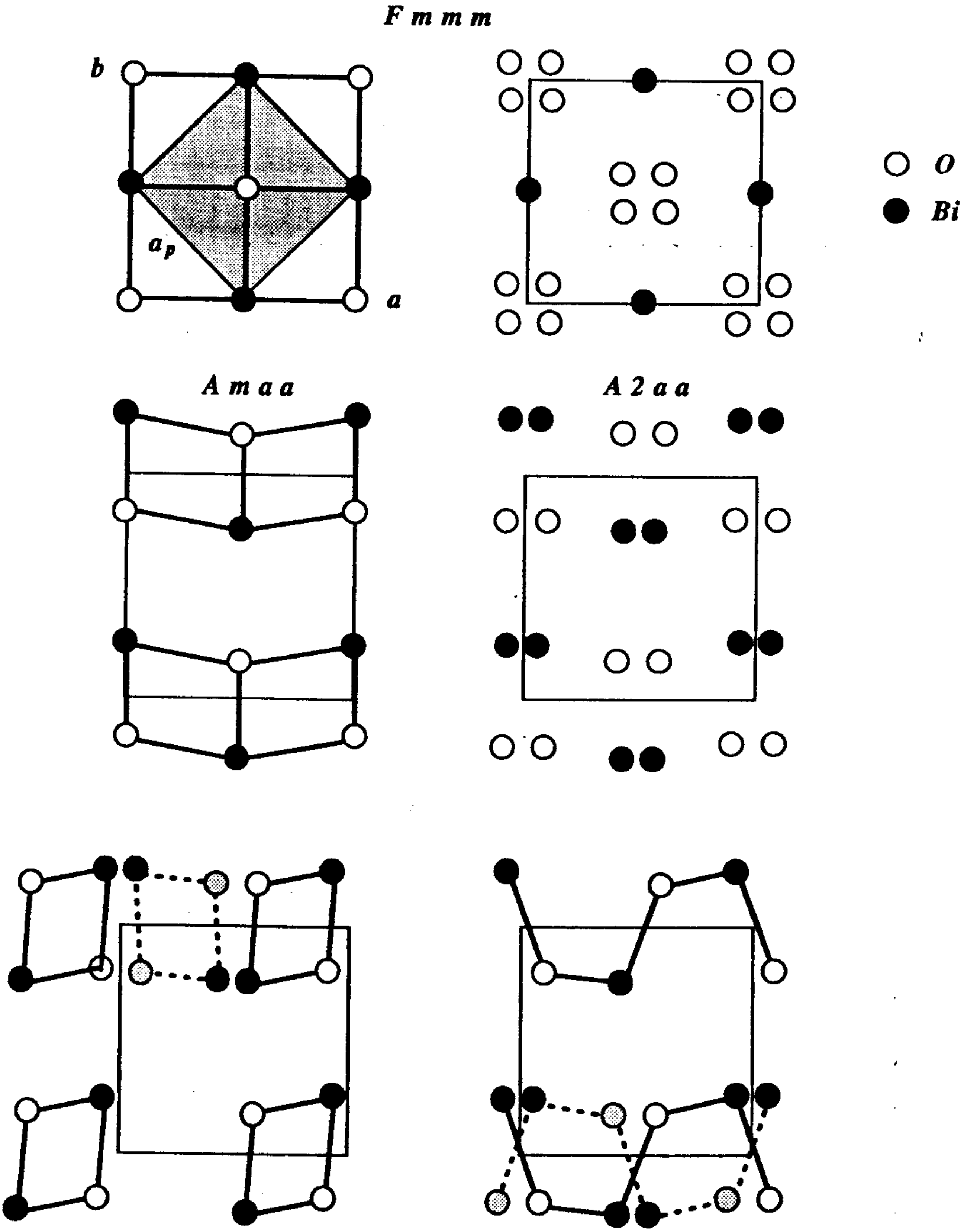

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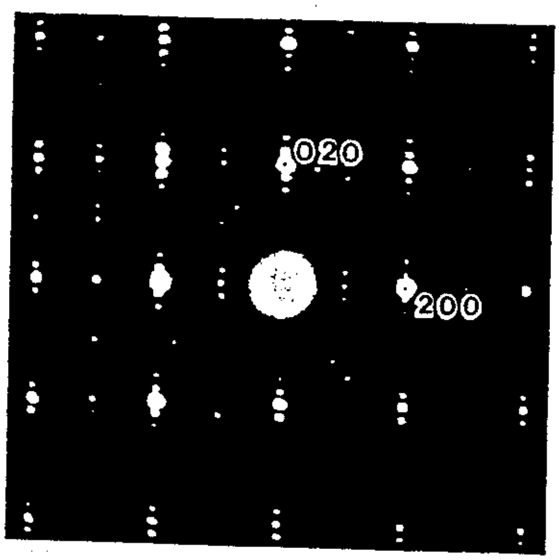
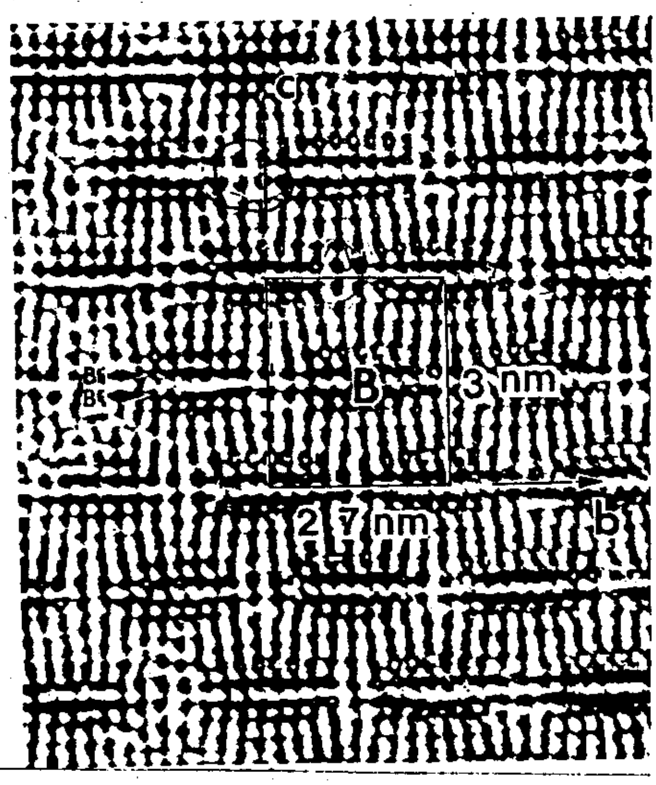


$Bi_2Sr_2CaCu_2O_8$



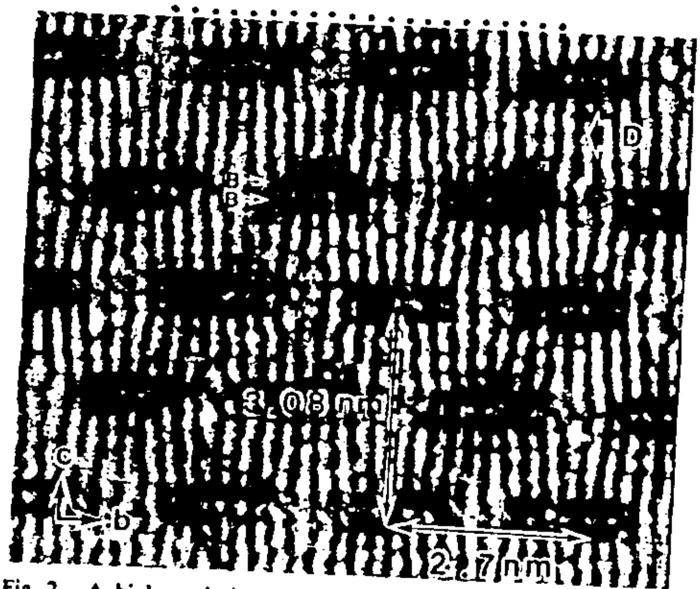
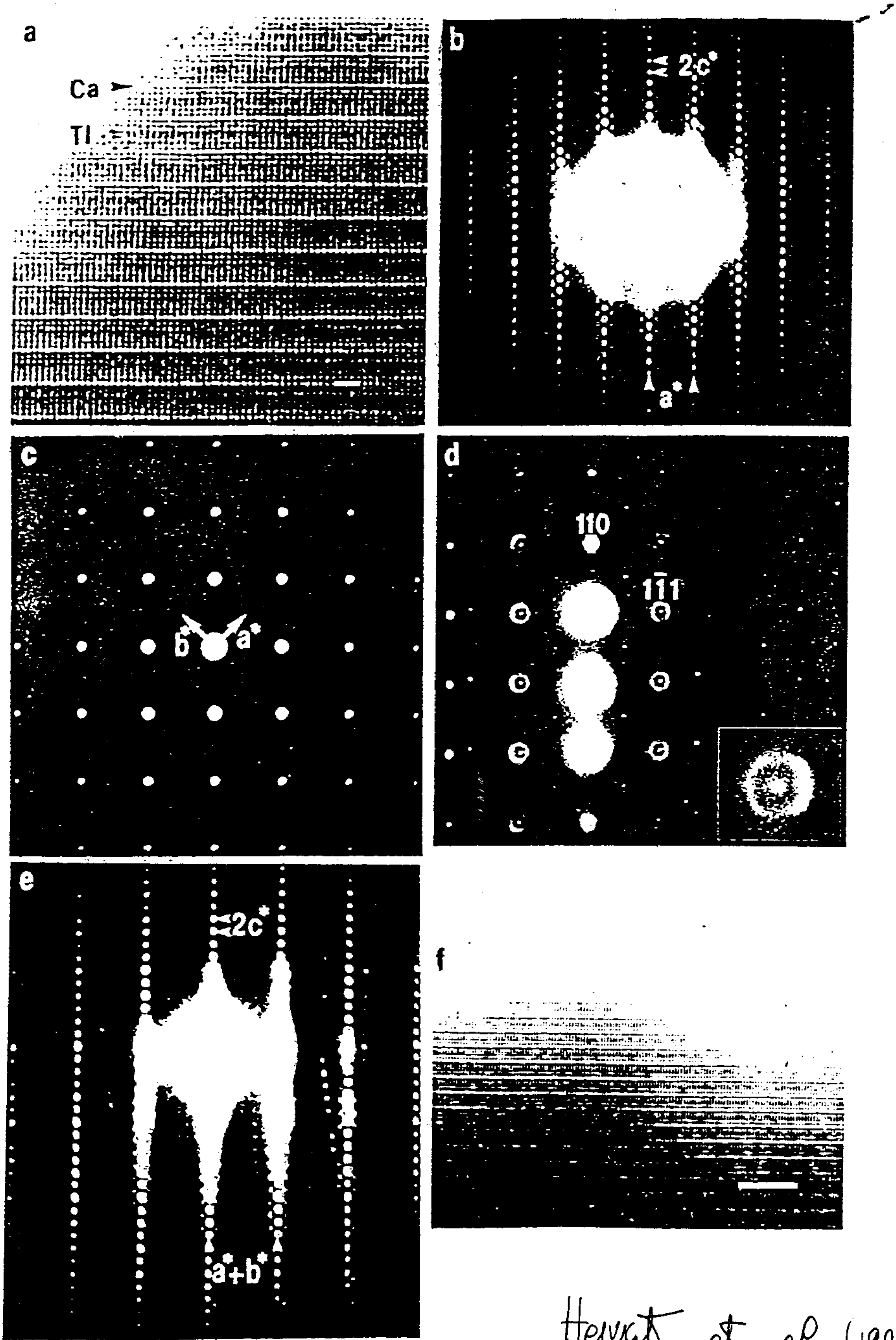


Fig. 2. A high-resolution electron micrograph viewed along the *a*-axis. Positions of the double Bi layers are indicated by the letters B.

Hirotsu et al., Jap. J. Appl. Phys. 27 (1988) L1869



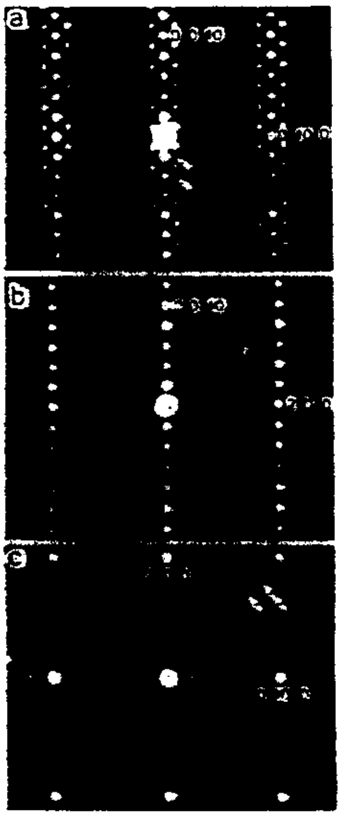
Hewat et. al (1988)

$Bi_2Sr_2Ca\,Cu_2O_8$

Typical features of the one–dimensionally modulated structures:

$$\mathbf{H} = h\boldsymbol{a}^* + k\,\boldsymbol{b}^* + l\boldsymbol{c}^* + m\mathbf{k} = \mathbf{G} + m\mathbf{k}$$

in this case: $\mathbf{k} = (1/p)\,\boldsymbol{a}^*$ $\quad$ p = 4.75 – 5



Y. Hirotsu et al., *Jpn. J. Appl. Phys.*, **27** (1988) L 1870

Origin of structural modulation in BSCCO

proposed models:

- ordering of the orientation of the Bi^{3+} lone pair
  [Zandbergen et al. (1988)]
- ordering of Sr vacancies
  [Cheetam et al. (1988)]
- additional oxygen in BiO planes
  [Zandbergen et aL (1988)]
  [E.A. Hewat et al. (1988)]
- ordering of Bi depleted zones
  [Maeda & Matsui (1988)]

All these models are qualitative and not completely satisfactory.

STRUCTURAL ANALYSIS OF A MODULATED PHASE

SUPERSPACE FORMALISM AND SYMMETRY:

- the unique approach for incommensurate structures
- succesfully employed also for commensurately modulated structures

PRO : reduction of the independent structural parameters

CONTRA : no generalized computer programs for crystal structure analysis

3D FORMALISM AND SYMMETRY:

- applicable *only* to commensurately modulated structures
- structure analyzed as a superstructure based on a conventional 3D space group

PRO : generalized computer programs

CONTRA : large number of structural parameters
correlations introduced by pseudo–symmetry

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Structural modulation in $Bi_2Sr_2CaCu_2O_8$: quantitative structural determinations.

Three– dimensional approach

– Calestani el al. (1989)

superstructure $A=5a$, $B=b$, $C=c$

space group: $P\,n\,n\,n$

– Tarascon et al. (1989)

indirect study $Bi_{10}Sr_{15}Fe_{10}O_{46}$

superstructure $A=5a$, $B=b$, $C=c$

space group: $B\,2\,2\,2$

Four–dimensional formalism and simmetry

– Petricek et al. (1990) space group: $M^{A\,2\,a\,a}_{-1\,1\,1}$

- linear displacement of O atoms in the BiO layer vs. unit cell position along the *a* axis
- possible insertion of extra oxygen at the end of the modulation period
- static disorder for Bi?

– Kan (1990) space group: $N^{B\,b\,2\,b}_{1\,1\,1}$

$a \longleftrightarrow b$

- no evidence for extra oxygen
- modulation due to lattice mismatch
- cationic vacancies and substitutions

COMMENSURATE MODEL FOR $Bi_2Sr_2Ca\,Cu_2O_8$ IN THE *P n n n* SPACE GROUP BASED ON SINGLE CRYSTAL X–RAY DIFFRACTION DATA

- modulation produced mainly by structural mismatch between perovskite and BiO layers which generate displacements in the BiO layer to create shorter BiO bonds
- bonds arrangement around Bi changes remarkably along the modulation period, suggesting the existence of a sort of charge modulation on the Bi atoms
- displacive modulation in *ab* plane fades going away from the BiO layers
- displacive modulation along the *c* axis is retained in all the layers
- no clear evidence of extra oxygen

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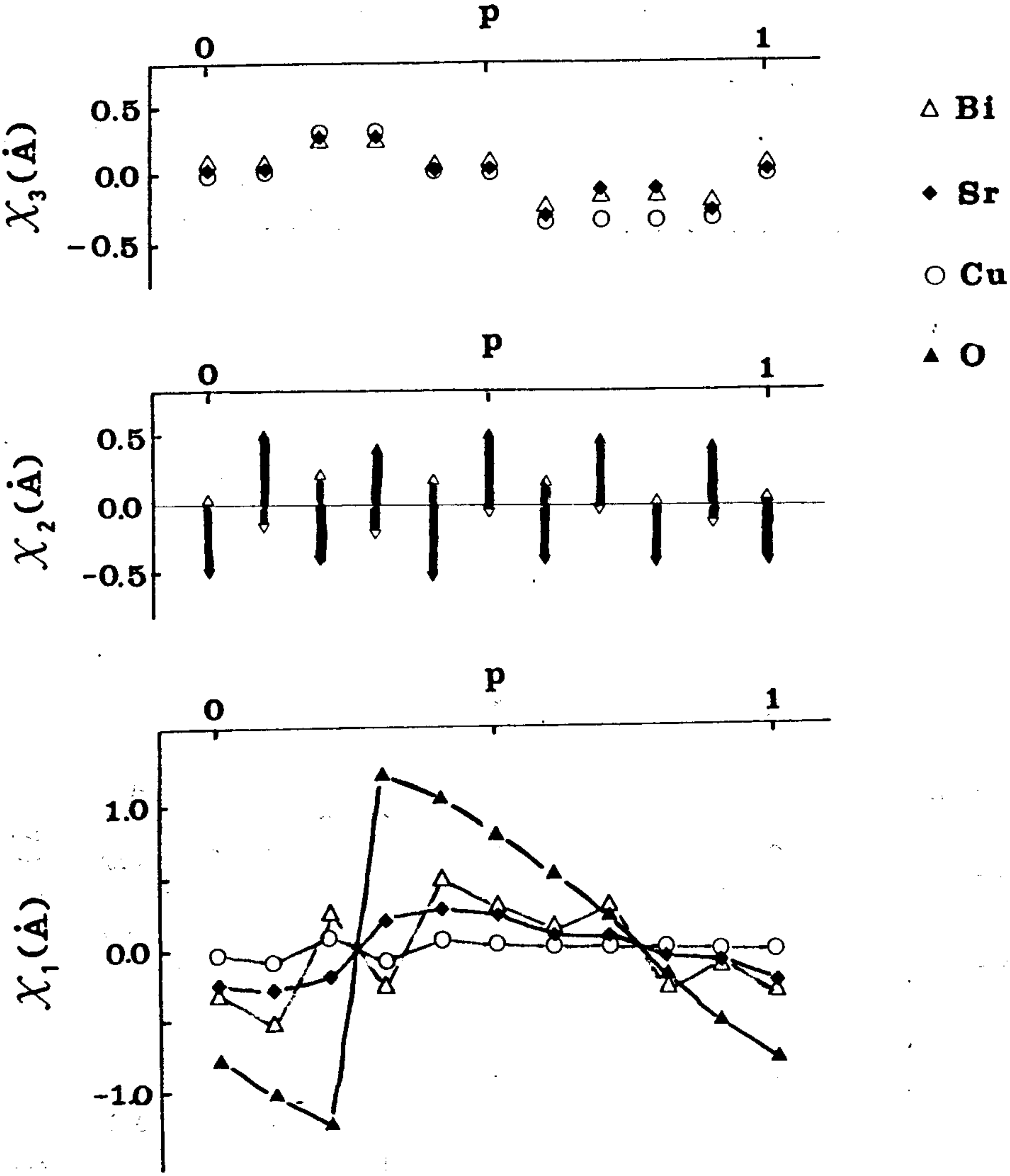
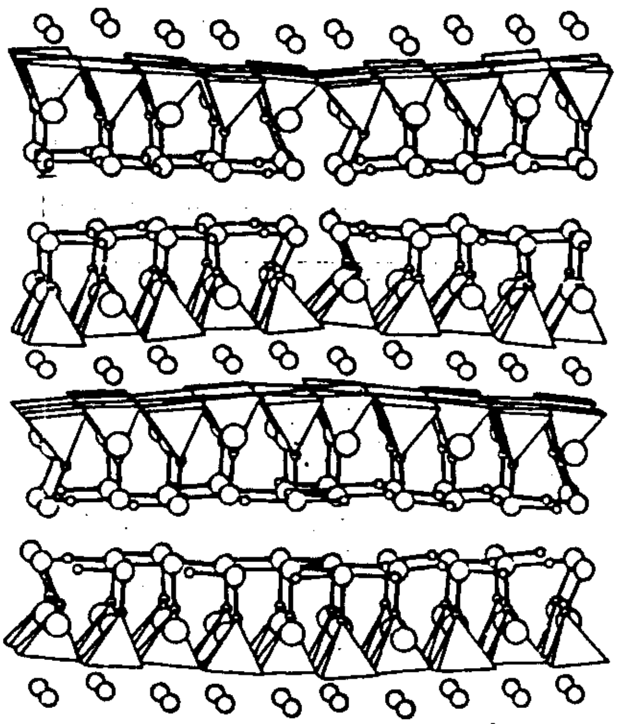
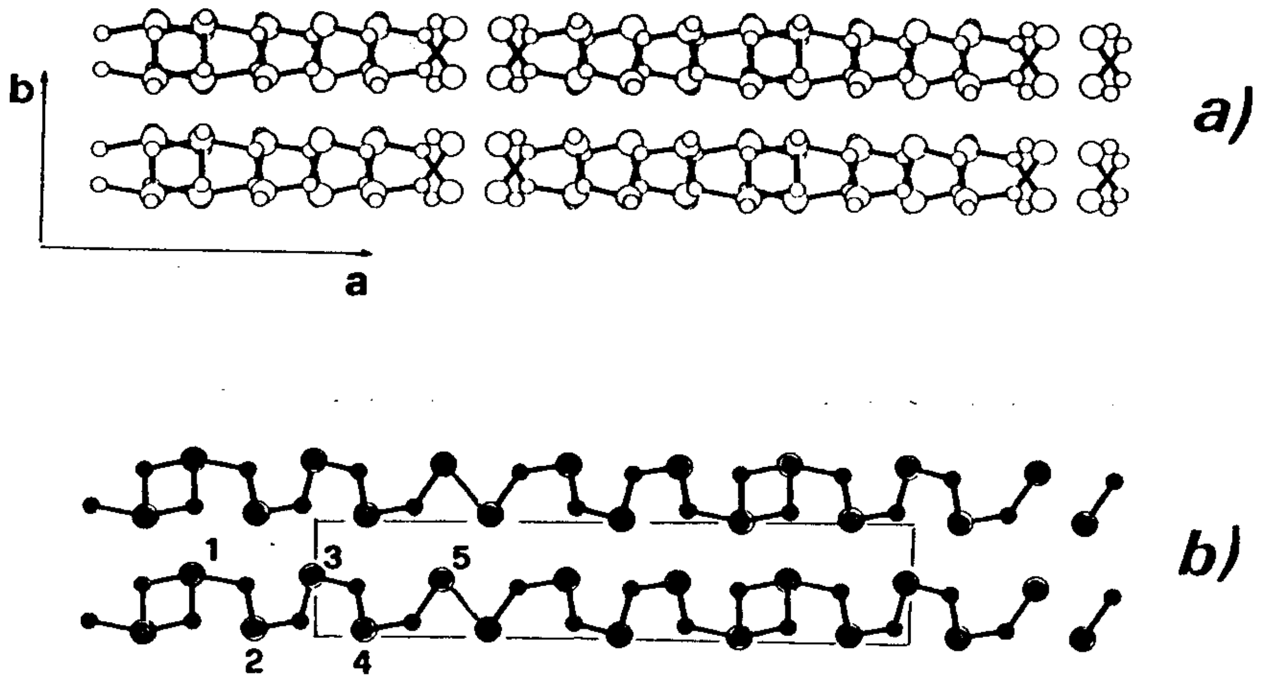
$$x_i = x_{oi} + \chi_i \qquad \chi_i = f(p)$$







b
a
a)
1
2
3
4
5
b)

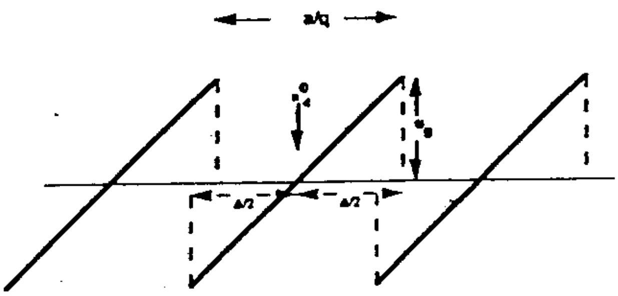
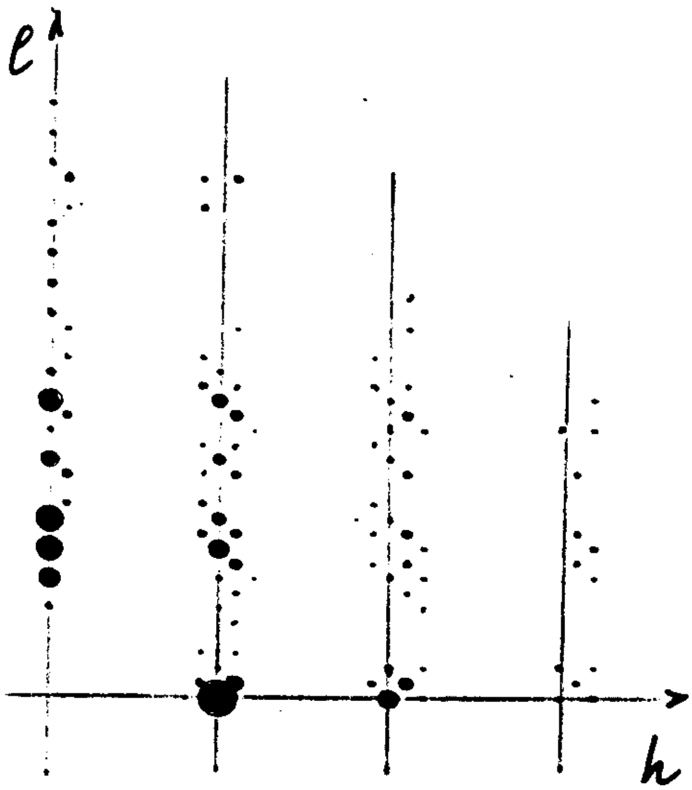


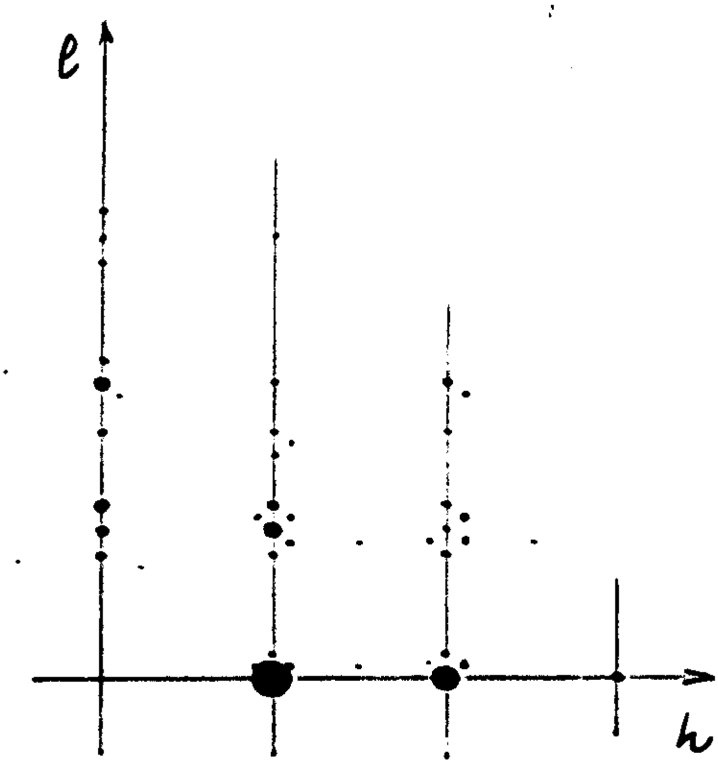
FIG. 3. The oxygen modulation model: displacement (vertical axis) vs unit-cell position along the a axis (horizontal axis).

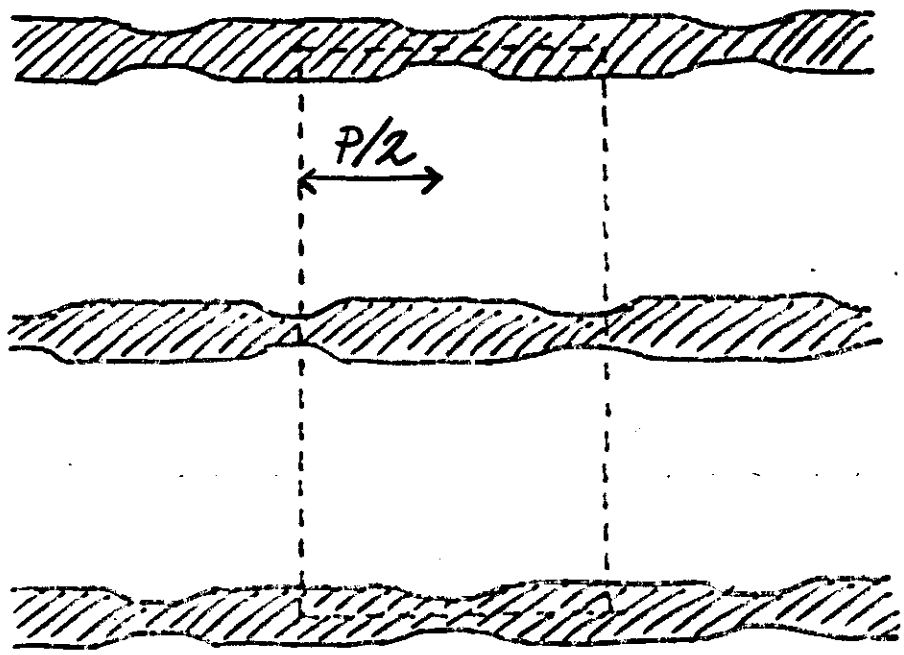
Petrucek et al

BSCCO
$n=2$

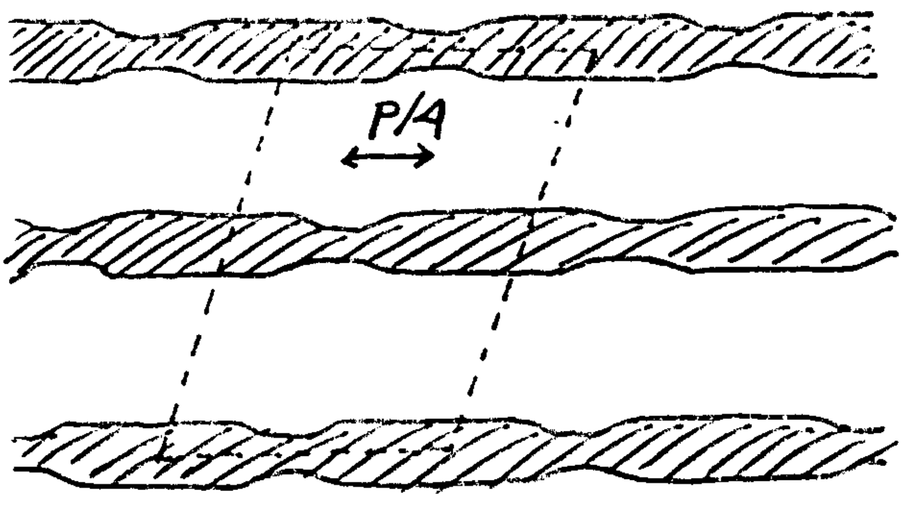


BSCCO
$n=3$





n = 2, 3



n = 1

Origin of superconductivity in BSCCO and TBCCO

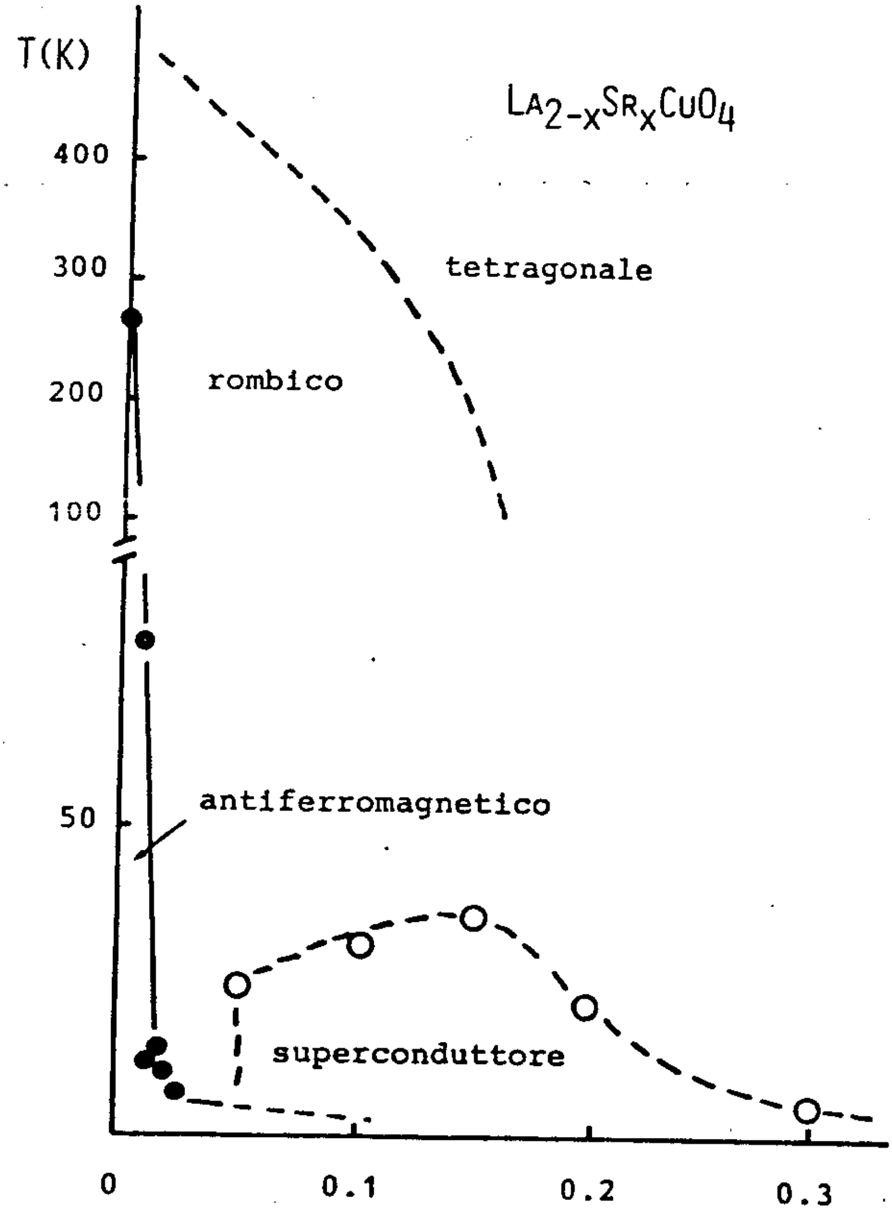
- BSCCO and TBCCO are very similar chemical compounds. Why not a similar origin of the superconductivity?

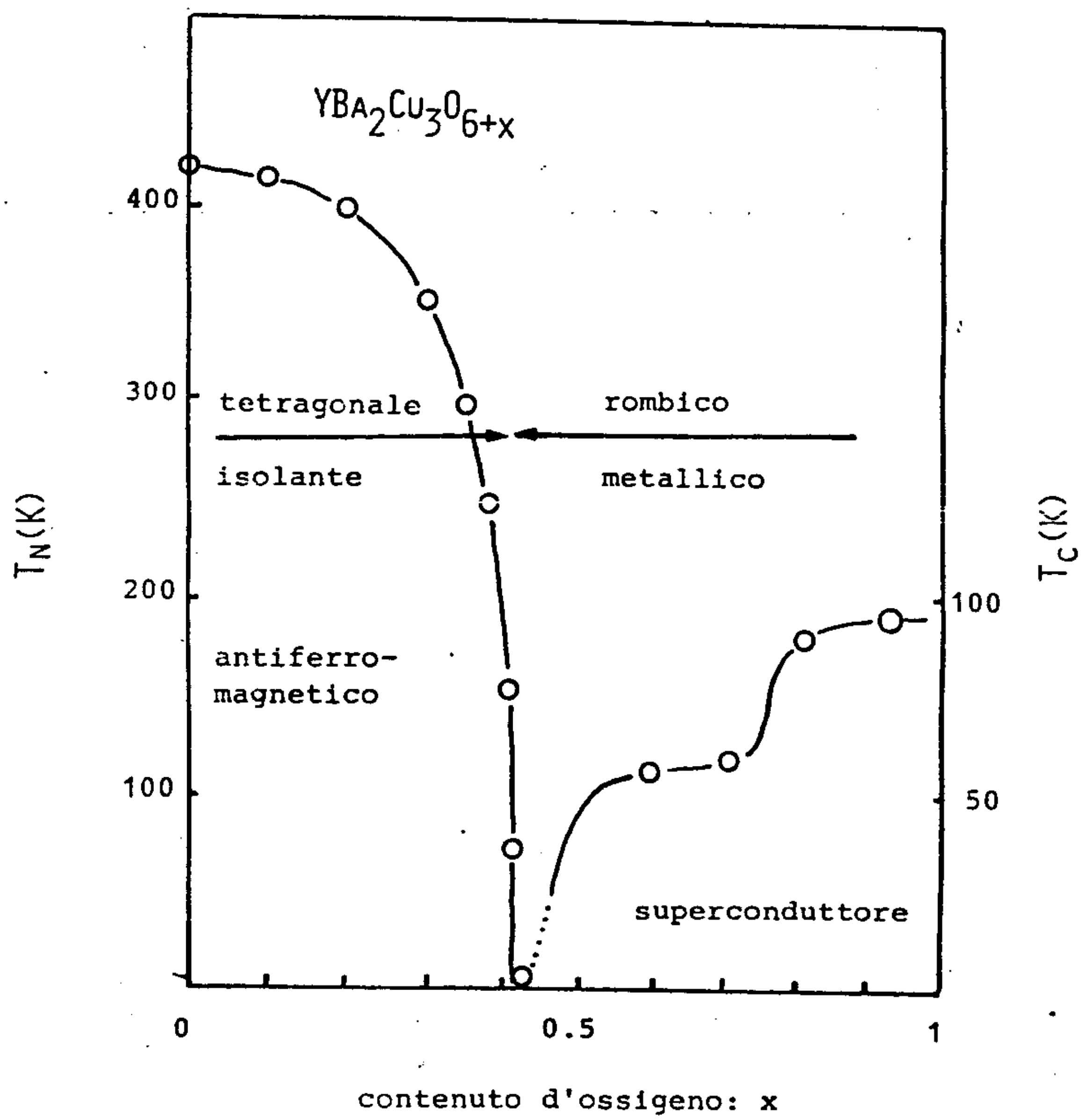
Structural differences:

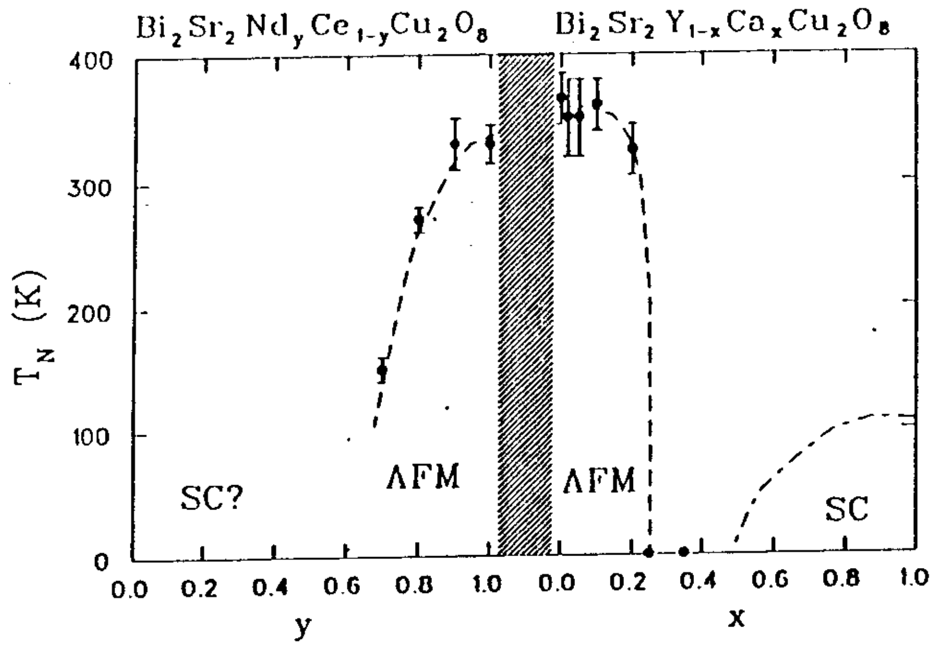
- The main structural difference consists in the existence of an important structural modulation in BSCCO which seems to be related more to the structural mismatch between perovskite and BiO layers and to the stereochemical requirements of Bi than to the eventual presence (not excluded *a priori*) of extra oxygen (why no important modulation in TBCCO?).
- A related structural difference is the weak chemical bond between adjacent BiO layers resulting in:
  - a longer *c* axis in BSCCO
  - no m=1 in BSCCO
  - preferential cleavage between the BiO layers in BSCCO.

Generalized proposed mechanism:

- Cationic vacancies or substitutions (*not so effective at least for BSCCO*)
- Oxygen non stoichiometry (δ *is positive or negative?*)
- Semimetallic character of the BiO (TlO) layers deriving from overlapping of interlayer bands (internal redox) (*may be general*)


T(K)
$La_{2-x}Sr_xCuO_4$
400
300
200
100
50
tetragonale
rombico
antiferromagnetico
superconduttore
0
0.1
0.2
0.3


$YBa_2Cu_3O_{6+x}$
400
300
200
100
tetragonale
isolante
rombico
metallico
antiferro-
magnetico
superconduttore
$T_N(K)$
$T_C(K)$
100
50
0
0.5
1
contenuto d'ossigeno: x



$Bi_2Sr_2Nd_yCe_{1-y}Cu_2O_8$
$Bi_2Sr_2Y_{1-x}Ca_xCu_2O_8$
T_N (K)
400
300
200
100
0
SC?
AFM
AFM
SC
0.0
0.2
0.4
0.6
0.8
1.0
0.0
0.2
0.4
0.6
0.8
1.0
y
x

$(Bi,Pb)_mSr_2Ca_{n-1}Cu_nO_{2n+m+2}$ (BPSCCO)

Partial substitution of Bi with Pb is studied for different reason:

- allows the preparation of single phase 2223 bulk samples
- increase the critical current density J_c
- seems to increase the T_c of the 2212 phase up to 90K
- change the structural modulation

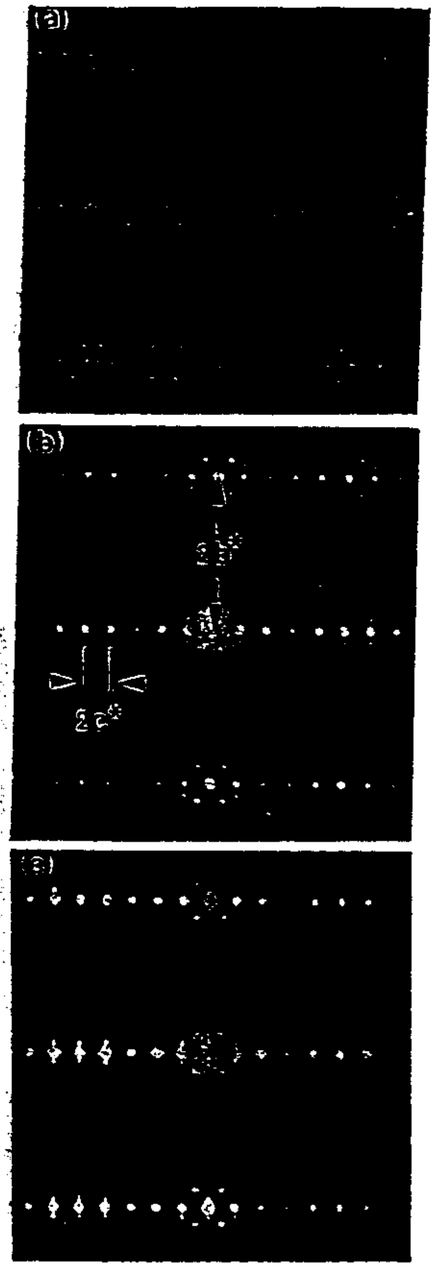


FIG. 3. Electron diffraction patterns along the [100] zone axis obtained from the (a) pure, (b) low-Pb, and (c) high-Pb samples. Note the presence of a new type of incommensurate superlattice reflections along b^* directly above (or below) the main lattice reflections. Some camera length is used for all diffraction patterns.

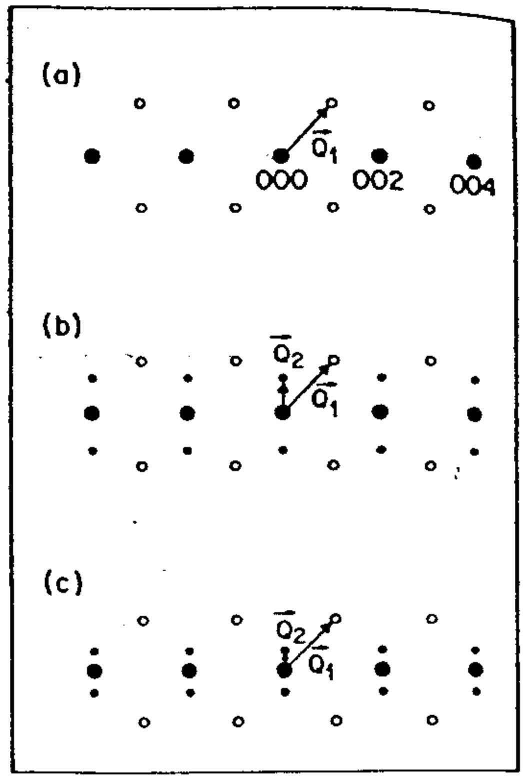
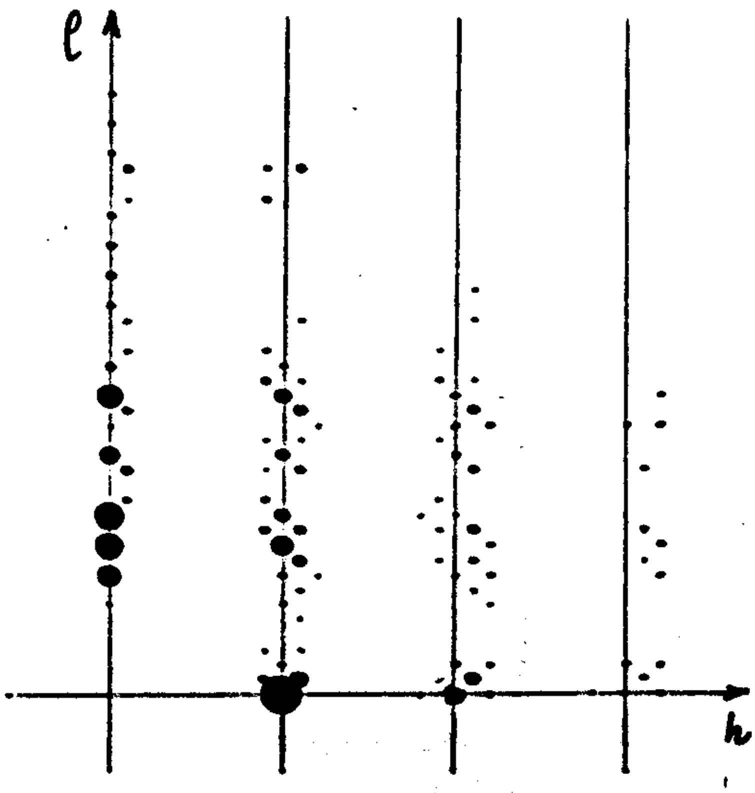


FIG. 4. Schematic illustrations of diffraction patterns shown in Figs. 3(a)–3(c). Diffraction spots due to the main sublattice, Q_1-type superlattice, and Q_2-type superlattice are represented by large filled circles, small open circles, and small filled circles, respectively.

BSCCO
n=2
BPSCCO (x<0.2)



BPSCCO (x>0.2)
n=2