What about Structure and Nonstoichiometry in Superconductive Layered Cuprates?

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An overview of the structural relationships and classification of the superconductive layered cuprates is presented here. The problems of nonstoichiometry extended defects in thallium cuprates and oxygen nonstoichiometry in $YBa_2Cu_3O_{7-\delta}$ are discussed. The issue of incommensurability in a great number of those phases is studied in connection with the stereoactivity of the $6s^2$ lone pair of Bi(III), Pb(II), and Tl(I). © 1990 Academic Press, Inc.

The discovery of superconductivity at high temperature in the system Ba–La–Cu–O (*1*) has greatly stimulated the investigation of copper-based oxides. A great number of new materials have indeed been isolated since the synthesis in 1980 of the mixed valent oxides $La_{2-x}A_xCuO_4$ (A = Ba, Sr) (*2, 3*), which several years later were found to be superconductors. Attention has been drawn very early on the important role of the low dimensionality of the structure in the superconductivity of those oxides (*4, 5*). It can now be stated that two factors—mixed valency of copper and bidimensional character of the structure—are very important factors governing the superconducting properties of those materials (*6*). The crystal chemistry of the layered oxides is very complex so that it can dramatically affect their superconducting properties. First we present here the structures of the layered copper oxides, whether superconductive or not, and their relationships leading to a classification which can

be used for the search of new compositions. Then, the following key points will be discussed: intergrowth phenomena, oxygen nonstoichiometry and its connection to the valency of the different elements, and structure incommensurability.

Structural Relationships and Classification of Layered Copper Oxides

The systematic investigation of oxides containing copper has led to the establishment of six series of copper oxides: these may be represented as La_2CuO_4-type oxides (*1–3, 7–12*), bismuth cuprates (*12–28*), the $YBa_2Cu_3O_7$ family (*29–36*), thallium cuprates (*37–54*), lead cuprates (*55–60*), and Nd_2CuO_4-type oxides (*61, 62*). All these oxides are characterized by a layered structure; despite their rather different complexities they are very closely related to each other so that a great number of them belong to the same structural family. La_2CuO_4-type oxides and Bi, Tl, and Pb cuprates can
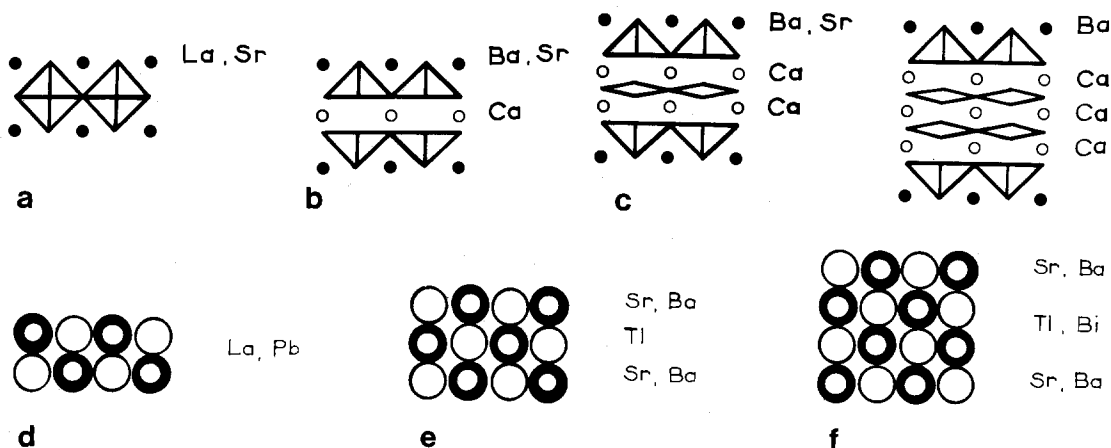
FIG. 1. Schematized structures of the perovskite (P) and rock salt (RS) layers forming the cuprates $(ACuO_{3-x})_m(AO)_n$. (a) $m = 1$ octahedral P layer; (b) $m = 2$ pyramidal P layers; (c) $= m \geq 3$ double pyramidal and square planar P layers; (d) $n = 1$ RS layer; (e) $n = 2$ RS layer; (f) $n = 3$ RS layers.

indeed be described as intergrowths of multiple oxygen-deficient perovskite slabs with multiple rock salt-type slabs according to the representation $[ACuO_{3-x}]_m^P[AO]_n^{RS}$ (P = perovskite; RS = rock salt; m, n are integers). These oxides may contain up to three types of perovskite slabs and three types of rock salt-type slabs:

The perovskite slabs can be octahedral (observed for $m = 1$), or formed of CuO_5 pyramids (observed for $m \geq 2$) or square planar CuO_4 groups, in addition to the CuO_5 pyramids (observed for $m \geq 3$). In the first case ($m = 1$) one expects no vacancies to appear on the anionic sites (Fig. 1a), leading to $x = 0$, whereas in the other cases the oxygen vacancies range from $x = 0.5$ (for $m = 2$ corresponding to only pyramidal layers) (Fig. 1b) to $x = 1$ (which is encountered for every additional copper layer corresponding to $m \geq 3$) (Fig. 1c).

The rock salt slabs are built up from AO layers. Rock salt-type slabs and perovskite slabs share always one AO layer so that one needs ($n + 1$) AO layers to form a multiple "n" rock salt slab. Thus, three kinds of rock salt slabs—single ($n = 1$; Fig. 1d),

double ($n = 2$; Fig. 1e), and triple ($n = 3$; Fig. 1f))—can be distinguished.

Consequently, these phases can be classified by use of the symbol [m, n], in which m and n represent the number of copper layers and the number of AO layers forming the perovskite and rock salt slabs, respectively. In such a representation single intergrowths, i.e., structures containing only one kind of slab—perovskite and rock salt, correspond to integral m and n values. When several types of perovskite or rock salt slabs coexist in the same structure, leading to multiple intergrowths, m and n are no longer integers.

Table I summarizes the different layered copper oxides corresponding to the [m, n] P/RS intergrowths which have been reported up to now. More than 30 compounds belong to this structural family. Moreover the "123" $YBa_2Cu_3O_7$-type superconductors (29–36) as well as the nonsuperconducting oxide $Ca_{0.86}Sr_{0.14}CuO_2$ (63), although not represented here, are also members of this series; they are oxygen-deficient perovskites, with an infinite number of copper layers and no rock salt-type

TABLE I

THE $[m, n]$-LAYERED CUPRATES: P/RS INTERGROWTHS

n			
m	1	2	3
1	[1, 1] La$_{2-x}$A$_x$CuO$_4$(A = Ca, Sr, Ba) T_c = 20–40 K $(1-3)$ La$_2$CuO$_4$ (10) Pb$_2$Sr$_{2-x}$La$_x$Cu$_2$O$_{6+\delta}$ (59) T_c = 30 K	[1, 2] TlBa$_2$CuO$_{5-\delta}$ (111) Nonsupercon- ductive TlSr$_2$CuO$_{5-\delta}$ (52) Traces Tl$_{1-x}$Pr$_x$Sr$_{2-y}$Pr$_y$CuO$_{5-\delta}$ (52) $T_c \approx$ 40 K $(x = 0.2; y = 0.4)$ Tl$_{0.5}$Pb$_{0.5}$Sr$_2$CuO$_{5-\delta}$ (56) Nonsu- perconductive TlBa$_{1+x}$La$_{1-x}$CuO$_{5-\delta}$ (51) $T_c \approx$ 50 K $(x = 0, 2)$	[1, 3] Tl$_2$Ba$_2$CuO$_6$ (15) T_c = 30 K Bi$_2$Sr$_2$CuO$_6$ (12) $T_c \approx$ 10–22 K
1, 5	[1.5, 1] Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_8$ T_c = 50 K $(x = 0.5)$ (55) Pb$_{2-x}$Bi$_x$Sr$_2$Y$_{1-y}$Ca$_y$Cu$_3$O$_8$ (58) T_c = 79 K $(x = 0, 6; y = 0.5, 1)$	—	—
2	[2, 1] La$_{2-x}$A$_{1+x}$Cu$_2$O$_6$ $(3, 64)$ $(A =$ Ca, Sr) Nonsuperconductive	[2, 2] TlBa$_2$Ca$_2$Cu$_2$O$_7$ (49) $T_c \approx$ 60 K TlSr$_2$CaCu$_2$O$_7$ (54) $T_c \approx$ 50 K Tl$_{0.5}$Pb$_{0.5}$Sr$_2$CaCu$_2$O$_7$ (53) $T_c \approx$ 85 K TlBa$_2$$LnCu_2O_7$ (112) $(Ln =$ Pr, Y, Nd) Nonsuperconductive Pb$_{0.5}$Sr$_{2.5}$Y$_{0.5}$Ca$_{0.5}$Cu$_2$O$_{7-\delta}$ $T_c \approx$ 59 K $(60, 113)$	[2, 3] Tl$_2$Ba$_2$CaCu$_2$O$_8$ $(39-42, 44)$ $T_c \approx$ 108 K Tl$_{3-4x/3}$Ba$_{1+x}$$LnCu_2O_8$ (71) $(x = 0, 25)$ $(Ln =$ Pr, Nd, Sm) Nonsu- perconductive Bi$_2$Sr$_2$CaCu$_2$O$_8$ (13) $T_c \approx$ 85 K Bi$_{2-x}$Pb$_x$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_8$ (98) $T_c \approx$ 85 K to nonsuperconduc- tive
3	[3, 1] PbBaYSrCu$_3$O$_8$ (57) Nonsuper- conductive	[3, 2] TlBa$_2$Ca$_2$Cu$_3$O$_9$ $(45, 48)$ $T_c \approx$ 120 K Tl$_{0.5}$Pb$_{0.5}$Sr$_2$Ca$_2$Cu$_3$O$_9$ (54) $T_c \approx$ 120 K	[3, 3] Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ $(39, 41, 44, 100)$ $T_c \approx$ 120 K Bi$_{2-x}$Pb$_x$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ (16) $T_c \approx$ 110 K
4	[4, 1] —	[4, 2] TlBa$_2$Ca$_3$Cu$_4$O$_{11}$ (114) $T_c \approx$ 110 K	[4, 3] Tl$_2$Ba$_2$Ca$_3$Cu$_4$O$_{12}$ (50) T_c = 104– 108 K
5	[5, 1] —	[5, 2] TlBa$_2$Ca$_4$Cu$_5$O$_{13}$ (115) T_c = 105 K	[5, 3] Tl$_2$Ba$_2$Ca$_4$Cu$_5$O$_{14}$ (116) T_c = 105 K

slab, corresponding to the symbol $[\infty, 0]$. Table I shows that only few of these ox- ides are not superconductors; never- theless among them the properties of La$_{2-x}$A$_{1+x}$Cu$_2$O$_6$ $(3, 64)$ and PbBaYSrCu$_3$O$_8$ (57) are really surprising since both com- pounds exhibit conditions required for su- perconductivity, bidimensional structure (Fig. 2), and mixed valency of copper. An- other striking feature concerns the disposi- tion of the cuprates in the columns accord- ing to the nature of the A cations; one
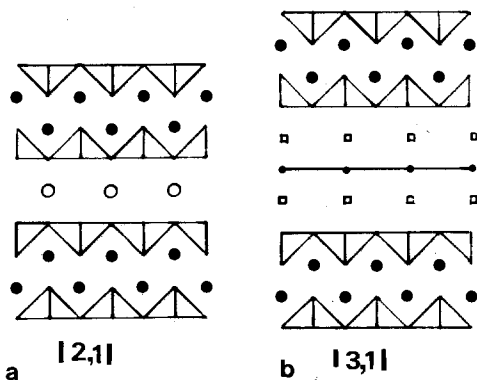
FIG. 2. Structure of two nonsuperconducting layered cuprates. (a) [2, 1], $La_{2-x}A_{1+x}Cu_2O_6$; (b) [3, 1], $PbBaYSrCu_3O_8$.

observes that the $[m, 1]$ compounds are found only in rare earth and lead cuprates, whereas thallium oxides form two series $[m, 2]$ and $[m, 3]$. A third important point deals with the very rare occurrence of multiple intergrowths, the only such phases being the oxides $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_8$ (55) and $Pb_{2-x}Bi_xSr_2Y_{1-y}Ca_yCu_3O_8$ (58) whose structure (Fig. 3a) exhibits extra oxygen deficiency with respect to the classical intergrowth which would have the composition $Pb_2Sr_2YCu_3O_{10}$ (Fig. 3b). The oxygen deficiency is here much greater ($\delta = 2$) than expected due to the formation of univalent

copper having a twofold coordination. This latter phenomenon is also observed in the phase $Pb_2Sr_{2-x}La_xCu_2O_{6+\delta}$ (59) whose structure (Fig. 3d) consists of octahedral layers alternating with layers of CuO_2 rods.

Besides this huge family, three other cuprates with a layered structure are worth describing: (i) the 80 K superconductor $YBa_2Cu_4O_8$ first observed as a defect (65) and synthesized as a pure superconductive phase (66), (ii) the Nd_2CuO_4-type oxides (61) which have been recently doped with cerium leading to superconductivity at 22 K (62, 67), and (iii) the oxides $Tl_{1+x}A_{2-y}Ln_2Cu_2O_9$ (68) which do not superconduct. All these compounds have structures closely related to those of the $[m, n]$ intergrowths described above. The structure of $YBa_2Cu_4O_8$ (Fig. 4a) is derived from that of $YBa_2Cu_3O_7$ (Fig. 4b) by considering a hypothetical structure "$YBa_2Cu_4O_9$" (Fig. 4c) in which double rows of corner-sharing CuO_4 square planar groups replace the single rows observed for $YBa_2Cu_3O_7$; then a simple shearing phenomenon produces the double rows of edge-sharing CuO_4 groups. A large family of intergrowths between $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ can be expected, with the general formula $(YBa_2Cu_3O_7)_n$ $(YBa_2Cu_4O_8)_{n'}$, whose first member ($n = n' = 1$) has already been synthesized (69).
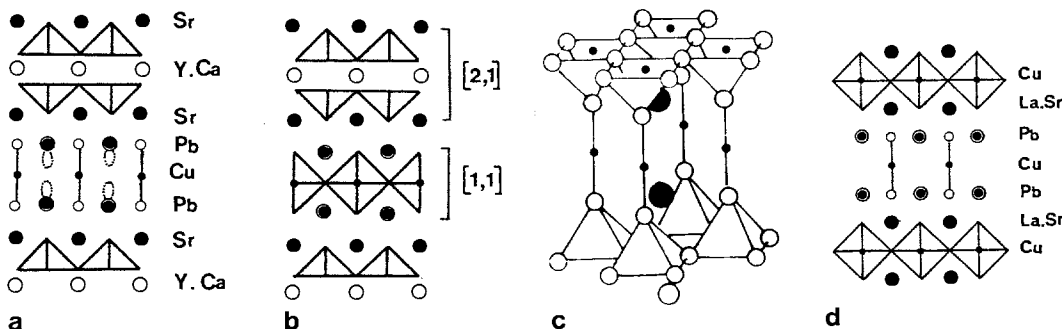
FIG. 3. Schematized structures of (a) [1.5, 1], $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_8$; (b) [1.5, 1], hypothetical "$Pb_2Sr_2YCu_3O_{10}$"; (c) [∞, 0], $YBa_2Cu_3O_6$; (d) [1, 1], $Pb_2Sr_{2-x}La_xCu_2O_6$.
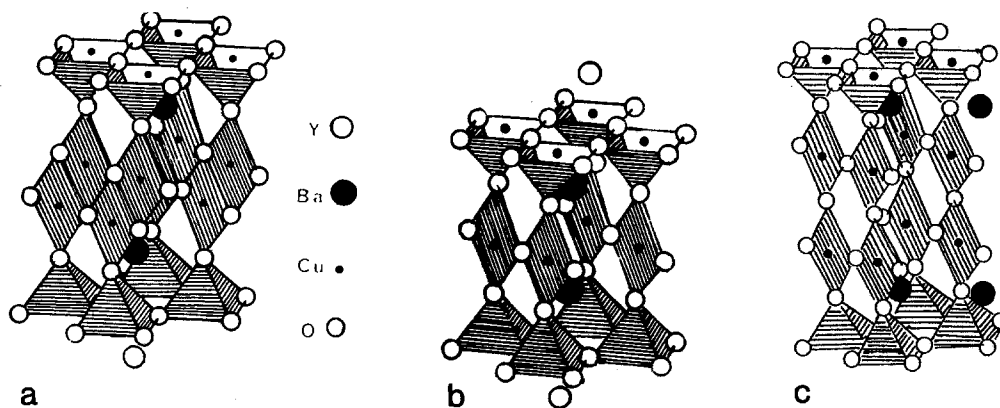
FIG. 4. Structures of (a) $YBa_2Cu_4O_8$; (b) $YBa_2Cu_3O_7$; (c) hypothetical $YBa_2Cu_4O_9$.

The Nd_2CuO_4-type structure (Fig. 5a) differs from the La_2CuO_4 structure (Fig. 5b) only by the positions of two oxygen atoms out of four: one recognizes in both structures identical $[CuO_2]_\infty$ layers of corner-sharing CuO_4 square planar groups interleaved in the same manner with identical layers of lanthanide cations. Nevertheless the displacement of some oxygen layers causes the CuO_6 octahedra of La_2CuO_4 to be replaced by CuO_4 square planar groups in Nd_2CuO_4. Moreover, one observes that Nd_2CuO_4 is built up from double fluorite-type layers (edge-sharing NdO_8 pseudo-cubic groups), whereas only simple fluorite type layers occur in La_2CuO_4. The bidimensional registry between these two structural types through the $[CuO_2]_\infty$ layers leads to the possibility of intergrowth between three types of layers: perovskite, rock salt, and fluorite. The recent synthesis of the oxides $Tl_{1+x}A_{2-y}Ln_2Cu_2O_9$ confirms this point of view. The structure of this latter phase (Fig. 6) consists indeed of the intergrowth of single copper pyramidal layers and double fluorite-type layers and double rock salt-type layers built up from thallium monolayers.
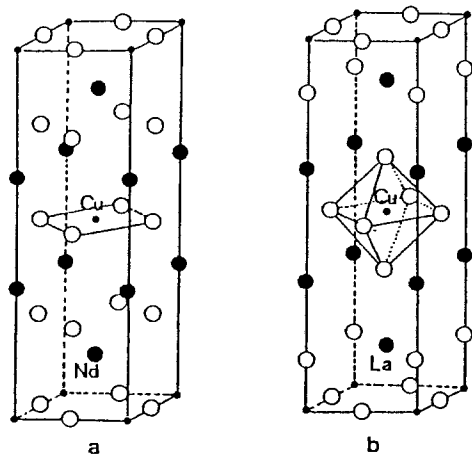
Nonstoichiometry: Intergrowth Defects and Oxygen Nonstoichiometry

1. Intergrowth Phenomena

The facile adaptability of perovskite and rock salt-type layers gives rise to a great variety of planar defects that can be observed which correspond to stacking faults of these two kinds of layers. This produces deviations from stoichiometry in the cation as the oxygen arrays. This phenomenon, which is rare in bismuth cuprates, is very
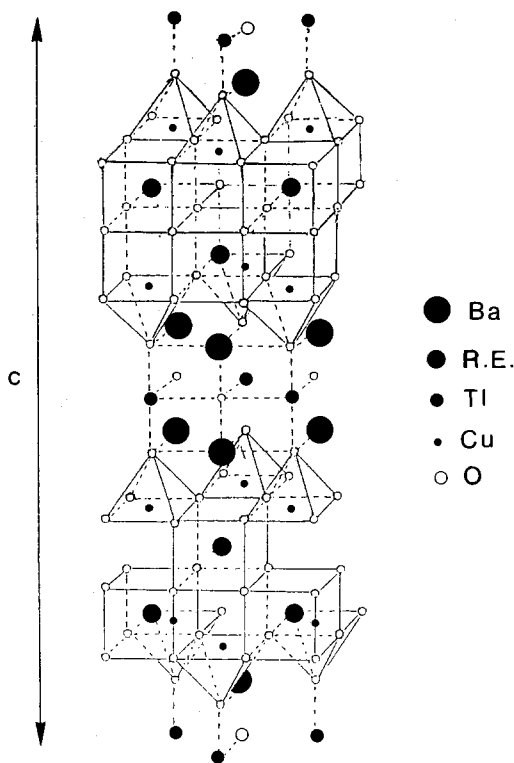

FIG. 5. Comparison of the structure of (a) Nd_2CuO_4 with that of (b) La_2CuO_4.

FIG. 6. Schematized structure of the oxide $Tl_{1+x}A_{2-y}Ln_2Cu_2O_9$ showing the triple intergrowths of perovskite, fluorite, and rock salt layers.

common in thallium derivatives due to the great volatility of thallium oxide, and, also, its ability to form various perovskite layers (m ranging from 1 to 5), and two sorts of rock salt-type layers (n = 2 and 3). These extended defects have been the subject of several studies by high resolution electron microscopy which will not be described here (cf. (70) and references included). Nevertheless, an attempt of classification of these defects is very useful since they can induce a dramatic modification of the superconducting properties of these materials.

The molar ratio (Tl + Ba)/(Ca + Cu) can be modified by two different mechanisms which correspond to the variation of the thickness either of the perovskite slabs or of rock salt-type slabs, respectively.

In the perovskite slabs such extended defects will be labeled as m', whereas the regular matrix will be m, with m' and m describing the number of copper layers forming the perovskite slabs in the defect and in the matrix, respectively. The m' defects are rarely observed in the $m = 1$ or 2 matrix and in that case they generally differ from m by 1 unit ($m \pm 1$). By contrast, for high m values the m' value can differ from m by several units as schematized for $Tl_2Ba_2Ca_3Cu_4O_{12}$ ($m' = 7$; $m = 4$) (Fig. 7); the number of m' defects increases with m.

Variations of the thickness of the rock salt-type slabs are very common in the thallium cuprates. They correspond to the formation of either $n' = 2$ defects (double rock salt-type layer) in a $n = 3$ matrix or $n' = 3$
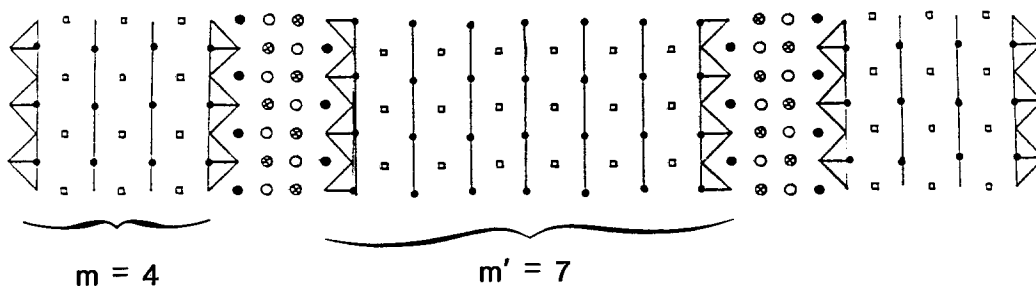

$m = 4$ $m' = 7$

FIG. 7. Schematized representation of the structure of a $m' = 7$ perovskite defect in a $m = 4$ matrix of $Tl_2Ba_2Ca_3Cu_4O_{12}$.
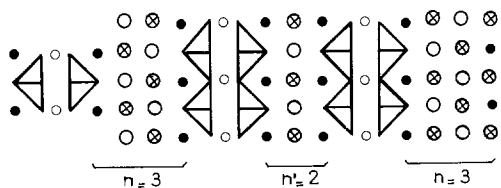
FIG. 8. Schematized representation of the structure of a $n' = 2$ rock salt defect in $n = 3$ matrix of the oxide $Tl_2Ba_2CaCu_2O_8$.

defects in a $n = 2$ matrix. One example of such a defect is schematized in Fig. 8. However, $n' = 1$ defects which correspond to the formation of single rock salt slabs in a $n = 2$ matrix are rarely observed. An interesting feature, which sometimes arises, concerns the introduction of additional $[CaO]_\infty$ layers in the rock salt-type slabs leading for instance to $n' = 5$ defects in a $n = 3$ matrix as schematized for Tl_2Ba_2Ca Cu_2O_8 (Fig. 9).

Aside from this variation of the ratio (Ba + Tl)/(Ca + Cu), another deviation from stoichiometry deals with thallium alone, which can indeed be substituted either for calcium or for barium. The former case is illustrated by complicated defects which are often observed by HREM; they correspond to the formation of $n' = 2$ defects (thallium monolayers) in a $n = 3$ matrix (thallium bilayers) and to the simultaneous
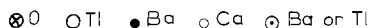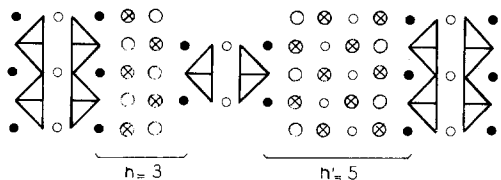
replacement of calcium layers by thallium layers, as schematized in Fig. 10a. The second case is observed in the case of the non-superconducting phase $Tl_{3-4x/3}Ba_{1+x}Ln$ Cu_2O_8 (71) which exhibits the [2, 3] structure (Fig. 10b); in that compound a significant amount of thallium ($x = 0.25$) is located on barium sites; interatomic distances suggest that a fraction of thallium is in the univalent state.

2. Oxygen Nonstoichiometry: The Orthorhombic Superconductor $YBa_2Cu_3O_{7-\delta}$

The oxygen stoichiometry is one of the most important factors concerning in composition since it dictates the Cu(III)/Cu(II) ratio and consequently governs the superconducting properties of those materials. For most of these phases the oxygen non-

FIG. 9. Schematized representation of $n' = 5$ rock salt defect resulting from the intercalation of two CaO layers in a $n = 3$ matrix of $Tl_2Ba_2CaCu_2O_8$.
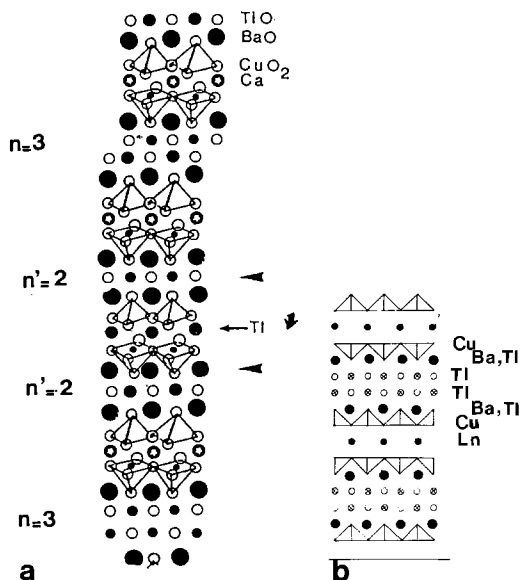

FIG. 10. Substitution of thallium for calcium and barium: (a) Double defect showing a $n' = 2$ defect (thallium monolayer) in a $n = 3$ matrix (thallium bilayers) followed by the replacement of a calcium layer by a thallium layer. (b) Structure of the [2, 3] nonsuperconducting phase $Tl_{2.7}Ba_{1.25}LnCu_2O_8$ showing the presence of Tl on the Ba sites.

stoichiometry problem is not really understood and cannot be fully described here. The orthorhombic superconductor $YBa_2Cu_3O_{7-\delta}$ which has been the subject of numerous studies is most fascinating.

The oxygen nonstoichiometry of this oxide can be understood by considering two limits, the orthorhombic 92 K superconducting phase $YBa_2Cu_3O_7$ ($\delta = 0$) (Fig. 4b) and the tetragonal nonsuperconducting phase $YBa_2Cu_3O_6$ ($\delta = 1$) (Fig. 3c). The latter is obtained from the former one by removing the oxygen atoms of the CuO_4 groups located at the copper level so that the pyramidal layers are linked through CuO_2 rods. Hence the "O_7 phase" is characterized by a Cu(II)–Cu(III) mixed valency, corresponding to the formulation $YBa_2Cu_2^{II}Cu^{III}O_7$, with a total delocalization of the holes over the copper–oxygen framework, whereas in $YBa_2Cu_3O_6$, one observes the mixed valency Cu(II)–Cu(I), involving localization of cations, with divalent copper in pyramidal configuration and univalent copper in twofold coordination, as represented by the formulation $YBa_2Cu_2^{II}Cu^{I}O_6$.

The deviation from "O_7" stoichiometry leading to the general composition $YBa_2Cu_3O_{7-\delta}$ strongly affects the superconducting properties of this material. Several groups have shown (35, 72–76) that T_c decreases as δ increases from 0 to 1. Nevertheless, it can be seen from Fig. 11 that this variation of T_c with δ differs greatly be-

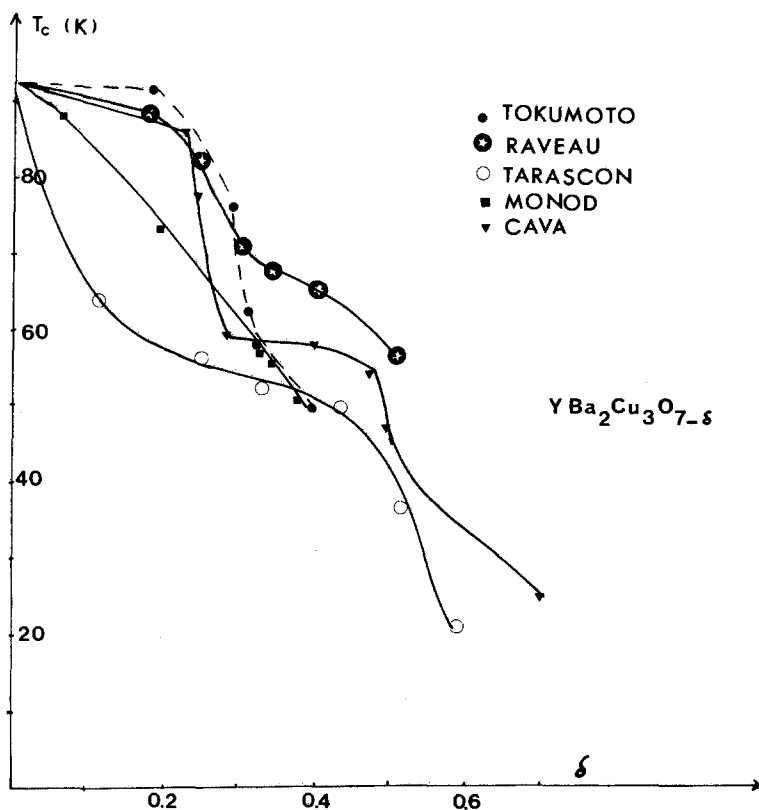

FIG. 11. Oxygen stoichiometry dependence of T_c in $YBa_2Cu_3O_{7-\delta}$ from different authors: Cava *et al.* (72), Monod *et al.* (73), Tarascon *et al.* (35), Tokumoto *et al.* (74), and Raveau *et al.* (75).
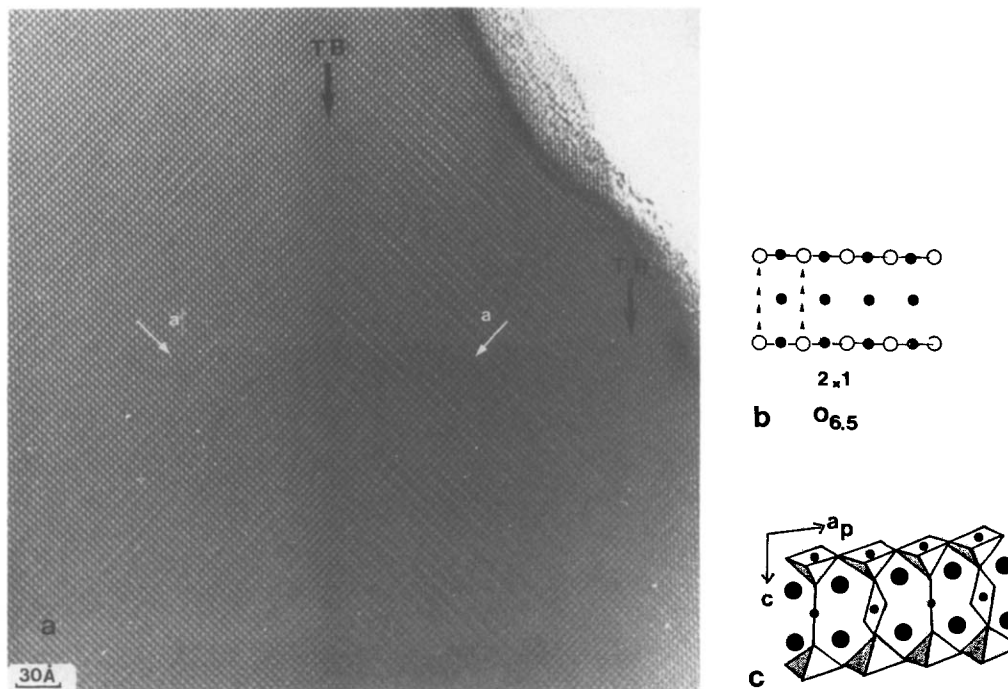
FIG. 12. $YBa_2Cu_3O_{7-\delta}$—Local $2a$ superstructure in the 60 K superconductor: (a) HREM image; (b) structural model projected along [001], showing the Cu 1 copper layer (the oxygen atoms are represented by an open circle, whereas the solid circle represents a CuO_2stick); (c) perspective view of the model.

tween the various groups. This type of behavior is not the result of the chance but corresponds to the fact that the arrangement of the oxygen vacancies in the structure depends upon the methodology of the synthesis. Clearly, order–disorder phenomena play an important role in the distribution of the oxygen vacancies. Thus, a simultaneous study by X-ray diffraction or neutron diffraction and HREM is necessary to elucidate these phenomena. We expose here mainly the results we have obtained by electron microscopy in Caen. An interesting example is that of the 60 K superconductors obtained for δ = 0.37–0.45. For those compositions, local superstructures were observed (77) along [100], [210], and [310] directions.

Local $2a$ superstructures are often en-

countered (Fig. 12a), without any change in the c parameter. Also, doubling of the a parameter is sometimes associated with a doubling of the c parameter. Such $2a \times 2c$ superstructures are shown in Fig. 13a; it can be seen that the contrast consists of one bright dot out of two along $\vec{c}$ in each triple copper layer, this contrast being translated from one layer to the adjacent one. Local $3a$ superstructures are also often observed (Fig. 14a). Such phenomena which correspond to local ordering of oxygen vacancies were also reported in electron diffraction studies by several authors (78–83, 117). However, some of these analysis are erroneous in our opinion because the analysis was based either on a wrong composition (81) or on an unrealistic threefold coordination of copper. Our model (77) for explain-
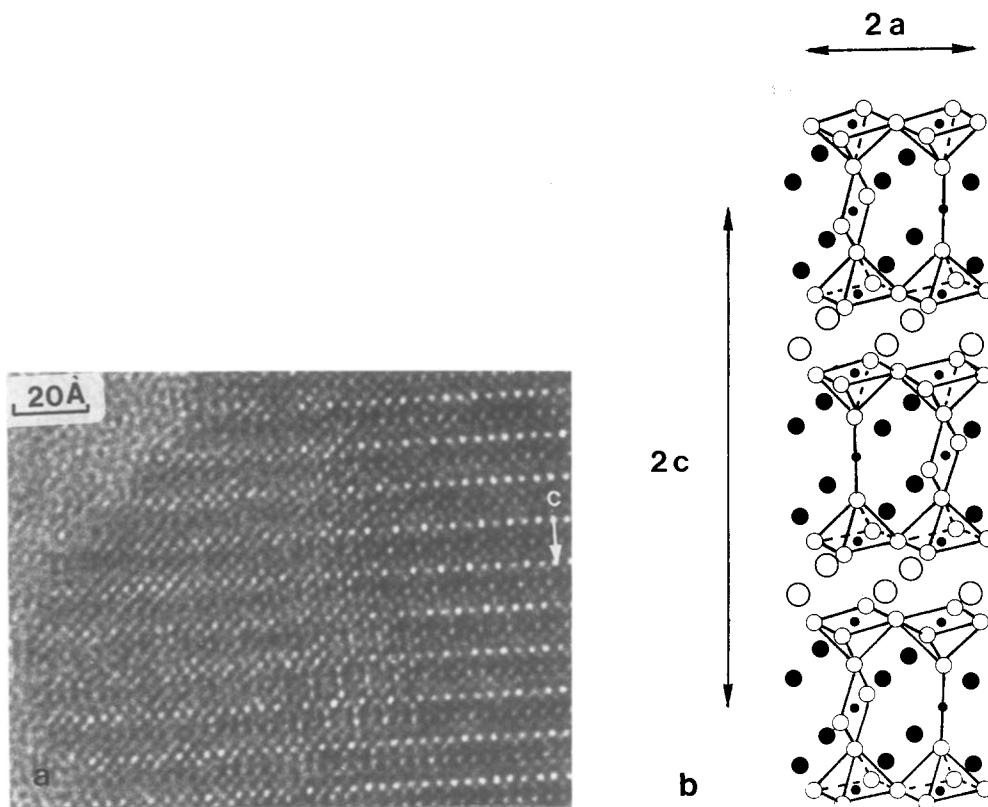
FIG. 13. $YBa_2Cu_3O_{7-\delta}$—$2a \times 2c$ superstructure: (a) HREM image; (b) idealized model corresponding to the formulation $YBa_2Cu_3O_{6.5}$.

ing these oxygen and vacancy orderings are based on the following points:

(i) Copper should have a usual coordination, i.e., twofold coordination for Cu(I) and four-, five-, or sixfold coordinations for Cu(II)–Cu(III).

(ii) The observed superstructures should have a composition as close as possible to the nominal investigated composition ($\delta \approx$ 0.37–0.45).

(iii) Copper should exhibit a disproportionation, according to the scheme 2Cu(II) $\Leftrightarrow$ Cu(I) + Cu(III), in order to explain its coordination. Such a hypothesis (84) is founded on X-ray absorption measurements (85–87) which clearly show the existence of Cu(I) in those oxides. Moreover,

this latter study shows that the Cu(I) content increases with δ and that the holes are more distributed among oxygen states rather than on copper sites leading to the configuration $Cu3d^9$ $\underline{L}$ ($\underline{L}$: ligand hole), which excludes the existence of $3d^8Cu^{3+}$ states.

In this model the multiplicity of the $\vec{a}$ axis, $n \times a$, implies that $(n - 1)$ $[Cu^{II,III}O_2]_\infty$ rows of corner-sharing CuO_4 groups parallel to $\vec{b}$ periodically alternate with one $[Cu^IO]_\infty$ row of Cu^IO_2 rods. Thus, the $2a$ superstructure consists of one single $[Cu^IO]_\infty$ row alternating with one $[CuO_2]_\infty$ row (Fig. 12b) according to the formulation $Y_2Ba_4[Cu_4^{II,III}O_{10}]^{PY}[Cu^{II,III}O_2]^{SQ}[Cu^IO]^L$ (δ = 0.50), whereas the $2a \times 2c$ superstruc-
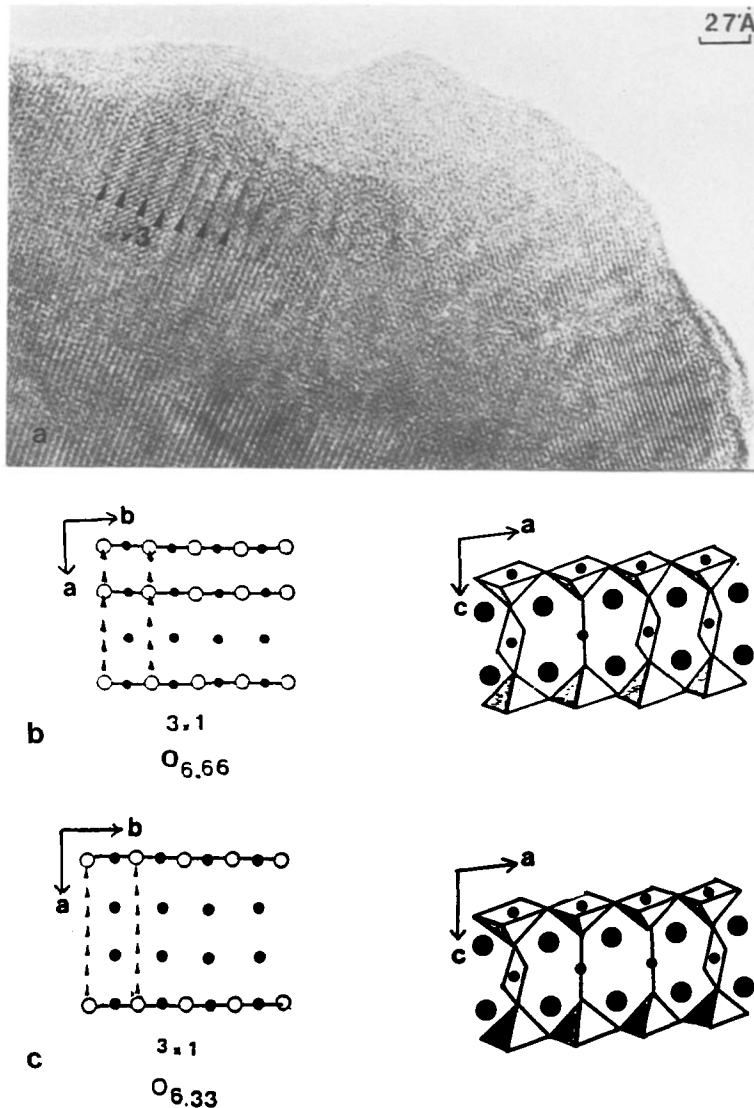
FIG. 14. $YBa_2Cu_3O_{7-\delta}$—Local $3a$ superstructure: (a) HREM image; (b) structural models showing the Cu 1 copper layer corresponding to two possible compositions $O_{6.66}$ (b) and $O_{6.33}$ (c) (the oxygen atoms are represented by an open circle, whereas the solid circle represents a CuO_2 stick).

ture which has the same formulation differs only by the fact that two successive layers along $\vec{c}$ are shifted with respect to each other (Fig. 13b). Similarly the $3a$ superstructure corresponds either to the periodic sequence of one single $[Cu^IO]_\infty$ row with $[CuO_2]_\infty$ rows parallel to $\vec{b}$ (Fig. 14c), corresponding to the formulation Y_3Ba_6 $[Cu_6^{II,III}O_{15}]^{PY}[Cu^{II,III}O_2]_2^{SQ}[Cu^IO]^L$ ($\delta = 0.33$), or to the sequence of one single $[CuO_2]_\infty$ row alternating with two $[Cu^IO]_\infty$ rows, according to the formulation Y_3Ba_6 $[Cu_6O_{15}]^{PY}[Cu^{II,III}O_2]^{SQ}(Cu^IO)_2^L$ ($\delta = 0.66$) (see Fig. 14b). Recently Reyes Gasga et al.

FIG. 15. $YBa_2Cu_3O_{7-\delta}$—Local superstructure along [110].

(88) have isolated single crystals with such superstructures; their simulation of the structure confirms the above models.
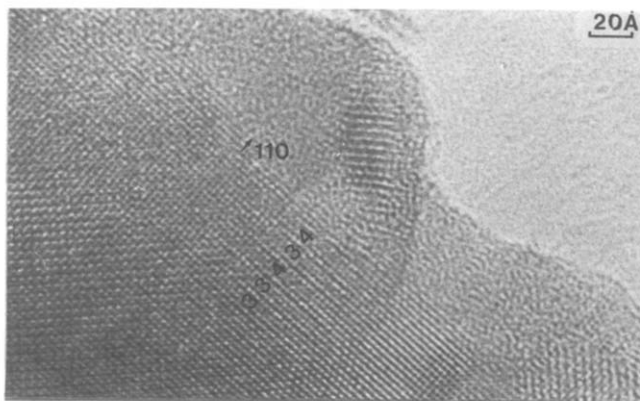
Additionally, one observes for $\delta = 0.37$–0.45 (78) other more complex local superstructures, such as those running along [110] (Fig. 15), or along [210] and [310] (Fig. 16). Models can easily be proposed for these supercells which invoke the generally accepted coordination of copper; for instance, in the $2a \times a\sqrt{10}$ superstructure (Fig. 16a) CuO_5 pyramids are lined up along $\vec{a}$, with alternating positions of the vertex which ensure the connection of segments parallel to $\vec{b}$, formed of two CuO_4 square

planar groups. This latter model can be generalized to various lengths of the $n \times CuO_4$ segments, the first one corresponding to a supercell $2a \times \sqrt{5}$ (along [210]), with $n = 1$ (Fig. 16b). Thus the n value can range from $n = 1$ (O_7) to $n = \infty$ ($O_{6.5}$) and the a and b parameters of the corresponding supercell are $2a \times a\sqrt{(1 + (n + 1)^2}$ with an oxygen content $O_{6.5+1/n+1}$. Moreover, such an ordering of the oxygen vacancies may also be accompanied by a slight displacement of the atoms with respect to the normal positions of the "stoichiometric" $YBa_2Cu_3O_7$ oxide, leading to a distortion of the cell. Thus, the oxygen nonstoichiometry in
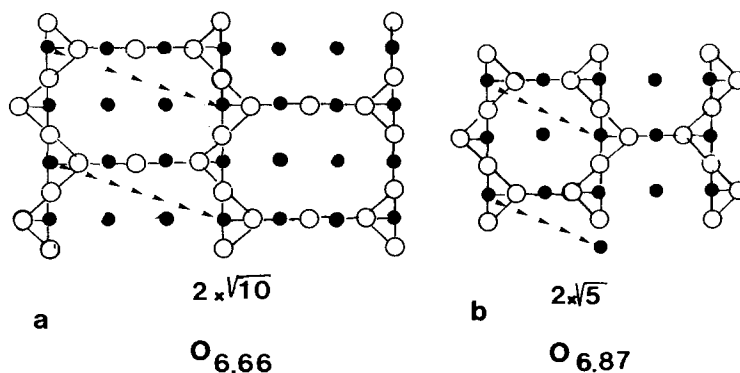

Fig. 16. Idealized models of supercells (a) $2a \times a\sqrt{10}$; (b) $2a \times a\sqrt{5}$.

$YBa_2Cu_3O_{7-\delta}$ can be understood in terms of a coexistence in the same crystal of ordered microdomains with variable oxygen compositions, in which the usual coordination of copper is maintained according to the formula $(YBa_2Cu_3^{II,III}O_7)_{1-\delta}(YBa_2Cu_3O_6)_\delta$. The homogeneity of the crystals, and their oxygen content, will then depend on the size of such domains. Clearly, perfect ordering of oxygen vacancies for intermediate δ values will only be obtained through long annealing times and by controlling the oxygen pressure to achieve only one type of ordering to a whole crystal. Usually, since the diffusion of oxygen through the crystal is so difficult, one will encounter this coexistence of various microdomains. Consequently, it is very likely that the plateau observed in T_c near 60 K corresponds to a particular predominant order, whereas the absence of this plateau for the same composition would be due to the coexistence of different microdomains of very small size with different oxygen contents.

Structure Incommensurability

Incommensurate satellites were reported by us for the first time in the electron diffraction patterns of $Bi_2Sr_2CuO_6$ (*12*). This phenomenon was then observed in all other bismuth cuprates (*14, 89–97*). Such satellites are located along the [100]* direction of the orthorhombic cell (Fig. 17a), but they can also appear along two directions at 90° (Fig. 17b). The HREM image of $Bi_2Sr_2CuO_6$ (Fig. 18) shows this modulation of the structure, which appears in the form of domains oriented at 90°; one can observe the undulations of the bismuth layers on the right part of the crystal and also the cleavage which takes place between two bismuth layers.

This incommensurability of the structure is not confined to bismuth cuprates. The solid solution $Bi_{2-x}Pb_xSr_2Ca_{1-x}Y_xCu_2O_8$ (*98*) which belongs to the [2, 3] type also shows incommensurate satellites on the E.D. patterns, ranging from $x = 0$ for the superconducting phase to $x = 1$ which is insulating. In that case the satellites along [100]* are rare. But other incommensurate satellites are observed which occur either along the $[310]_P$ direction of the perovskite subcell (Fig. 19a) for $q = 6.25$ or along [100] for $q = 3.65$ (Fig. 19b) or which are characterized by a multiple splitting of the spots (Fig. 19c). Another striking example is provided by the pure lead cuprate PbBaYSr Cu_3O_8 (*57*) which represents the [3, 1] member of the family but is not superconducting. The E.D. patterns of this latter
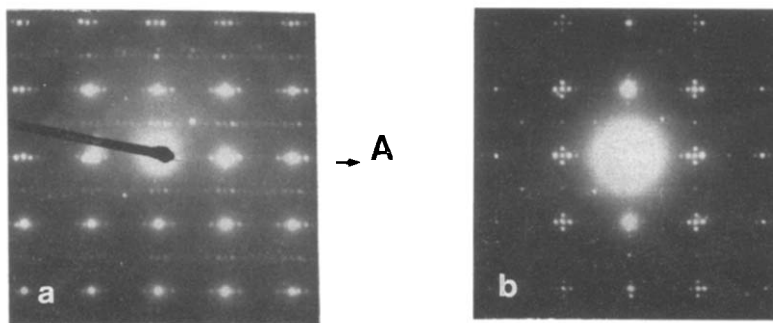

→ A

FIG. 17. E.D. patterns of the bismuth cuprate $Bi_2Sr_2CaCu_2O_8$ showing (a) satellites setting along [100]*; (b) satellites along two directions at 90°.
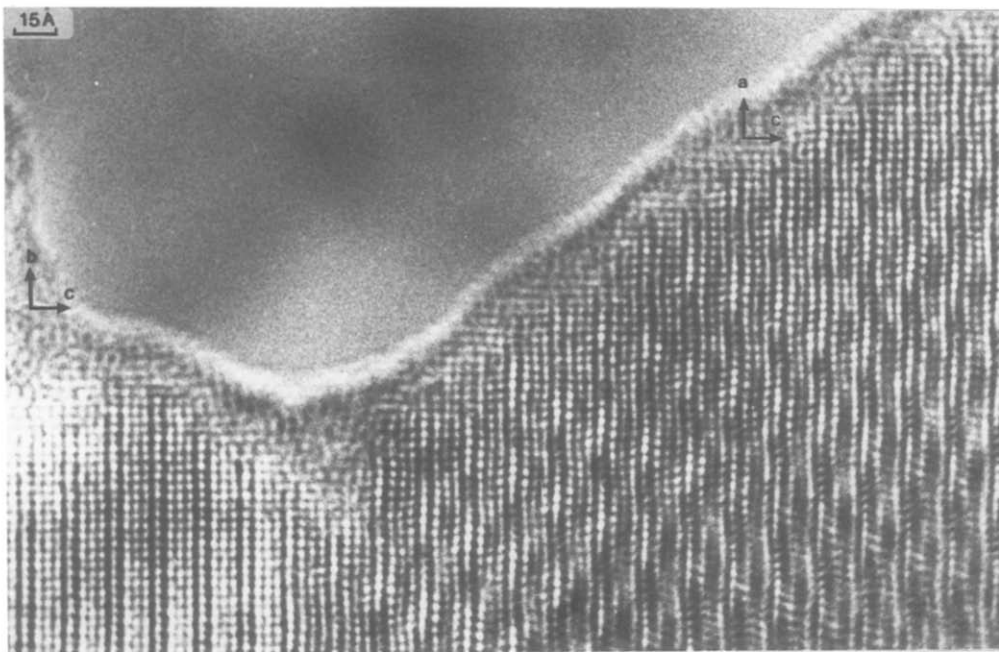
FIG. 18. HREM image of $Bi_2Sr_2CuO_6$. The waving of the bilayers can be observed on the right side of the micrograph ([010] orientation). On the left side, the 90°-oriented domain is observed ([100] orientation).

phase exhibit satellites which signal a bidimensional modulation (Fig. 20a), corresponding in fact to a superimposition of two systems of spots oriented at right angles. Both systems are located along [310]* and [110]*. For the most intense satellites the wavelength of the modulation is slightly variable and close to four times the d_{110} (2.8 Å) distance. In some crystals for longer exposure times, satellites in 1/8 position ($hh0$) are observed (Fig. 20b); extra spots are also obtained due to double diffraction phenomena. Two sets of satellites can be identified (Fig. 20c) from the [001] section. The incommensurate nature of the modulation is clearly visible from the [110] electron diffraction patterns (Fig. 21).

The thallium cuprates exhibit a different behavior. Some authors (99–105) do not observe satellites characteristic of an incommensurate structure in the classical superconductive thallium cuprates, whereas others (106–108) observe such satellites but with very weak intensities. In a recent comparative study of the two phases (71), $Tl_2Ba_2CaCu_2O_8$ and $Tl_{2.7}Ba_{1.25}PrCu_2O_8$ which belong to the [2, 3] structure, the first phase did not exhibit any satellites whereas, for the second, satellites were always clearly visible along zones which deviate from the ideal direction (Fig. 22). Moreover the satellites were located in a direction similar to that observed for bismuth cuprates (Fig. 17a), with a wave vector in the (110)* plane, but with a different symmetry (tetragonal instead of orthorhombic) and a different wavelength of the modulation close to six times d_{110}. This latter phase differs from other cuprates by the presence of an excess of thallium, located
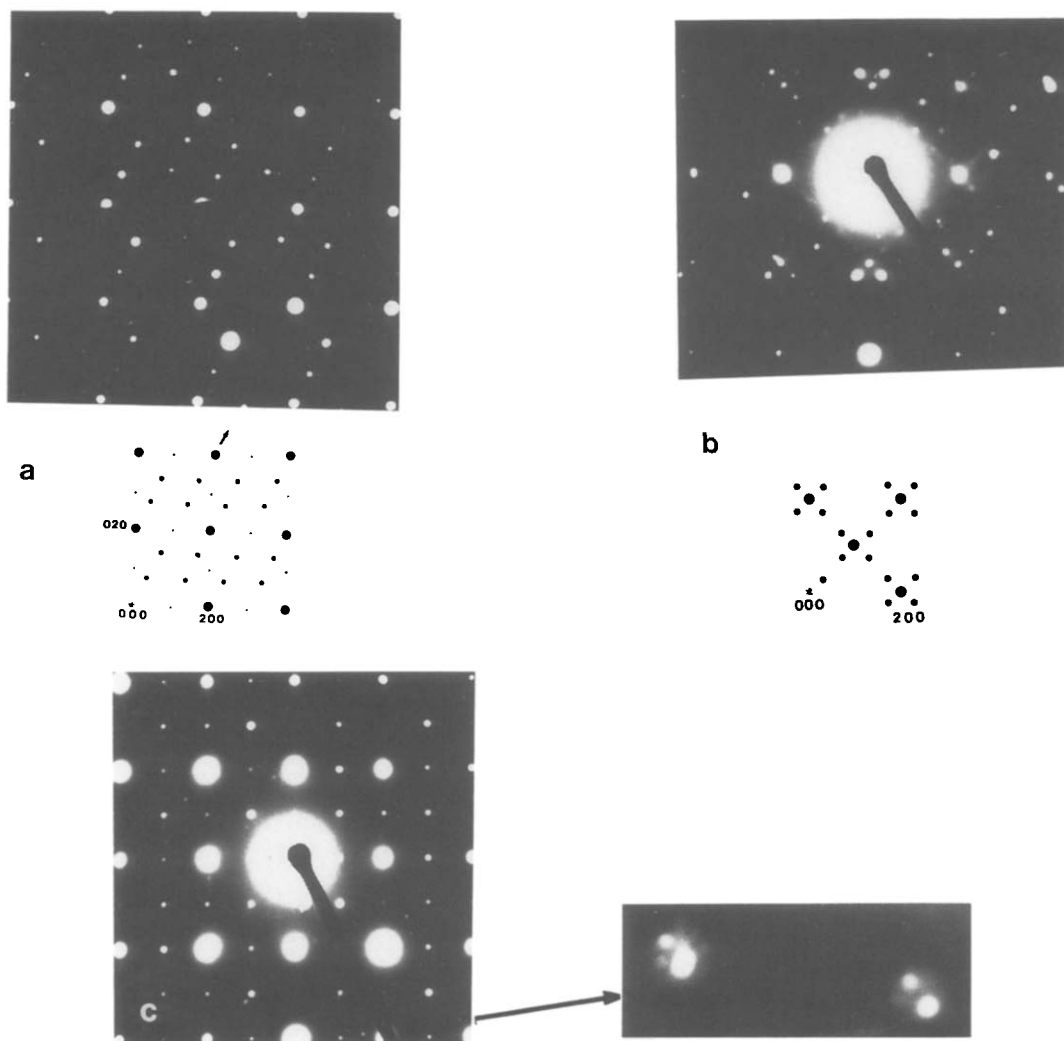
Fig. 19. [001] E.D. patterns observed in different areas of a crystal of $BiPbSr_2YCu_2O_8$. (a) Satellites set up along [310] of the perovskite subcell; (b) satellites set up along $[100]_p^*$ with small variations of parameters and microtwinning (enlargement of the two reflections are shown at the bottom).

in barium sites, which may be Tl(I). On the opposite the layered copper oxides which do not contain bismuth, lead, or thallium do not exhibit such incommensurate satellites.

From these observations, only a partial answer can be provided concerning the origin of incommensurate satellites and their relationships to superconductivity. Nevertheless it can be stated that this modulation of the structure is not related to the presence of copper layers, and does not result from superconductivity since isostructural oxides $Bi_2Sr_{3-x}Ca_xFe_2O_9$ (*109*) and Bi_2Sr_4 Fe_3O_{12} (*110*), in which FeO_6 octahedra replace the CuO_5 pyramids and CuO_4 square groups, exhibit very similar electron diffraction patterns. This particular behavior can be explained by the stereoactivity of

FIG. 20. (a) [001] E.D. pattern of PbBaYSrCu$_3$O$_8$ showing extra spots; (b) spots are visible when the zone is slightly deviated from the exact orientation; (c) two sets of satellites are identified; they are 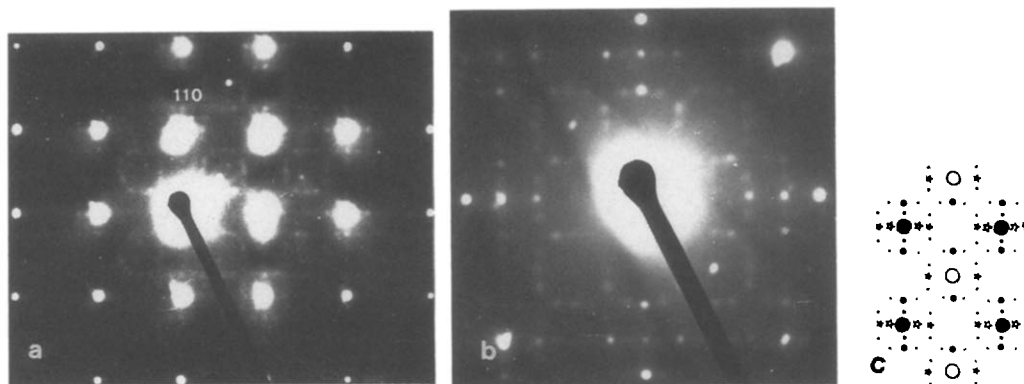characteristic of 90°-oriented domains. Basic spots at level 1/2 are represented as open circles; systems 1 and 2 ($\sim 4d_{110}$); systems 3 and 4 ($\sim 8d_{110}$); small spots, extra spots arising from double diffraction of systems 3 and 4 with 1 and 2 as second origin.

the $6s^2$ lone pair of Pb(II) and Bi(III) which tends to take the place of an anion and induces a distortion of the layers. It results in a nonperiodic displacement of the Bi(III) or Pb(II) cations and, consequently, of the atoms in the rock salt-type layers. The fact that such a phenomenon is very weak in thallium cuprates suggests either a slight nonstoichiometry involving the presence of small amounts of the lone pair cation Tl(I) or that the very small size of Tl(III) compared to barium induces such a distortion.
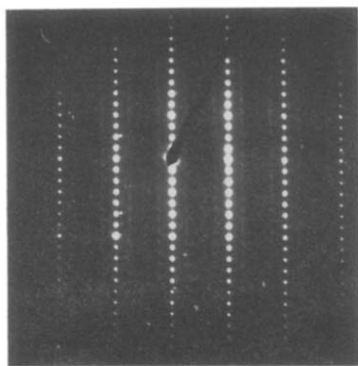
FIG. 21. [110] E.D. pattern of PbBaYSrCu$_3$O$_8$ with extra spots in incommensurate positions.

The fact that Tl$_{2.7}$Ba$_{1.25}$PrCu$_2$O$_8$ exhibits much stronger satellites suggests that the Tl(I) cation plays a role in this phenomenon. This hypothesis of the role of the $6s^2$ lone pair in incommensurability is also supported by the recent studies of the two superconductive lead cuprates, Pb$_2$Sr$_2$Ca$_{0.5}$Y$_{0.5}$Cu$_3$O$_8$ (55) and Pb$_{0.5}$Sr$_{2.5}$Y$_{0.5}$Ca$_{0.5}$Cu$_2$O$_{7-\delta}$ (60). The fact that the first does not exhibit any incommensurability despite the presence of Pb(II) is easily explained by the structure of this phase (Fig. 3a). It can indeed be seen that the Pb(II) cations are located on the border of the rock salt-type layers, so that their $6s^2$ lone pair can extend between the Cu^{I}O$_2$ rods taking the place of the oxygen vacancies. Consequently, the rock salt layer is not distorted by the $6s^2$ lone pair. The second oxide Pb$_{0.5}$Sr$_{2.5}$Y$_{0.5}$Ca$_{0.5}$Cu$_2$O$_7$ exhibits behavior intermediate between that of YBaPbSrCu$_3$O$_8$ and Pb$_2$Sr$_2$Ca$_{0.5}$Y$_{0.5}$Cu$_3$O$_8$. One indeed observes satellites whose intensity varies from one crystal to the other and which are always observed in the same plane of the reciprocal space (010) (or (100)), but with variable direction and wavelengths of the modulation. Moreover,
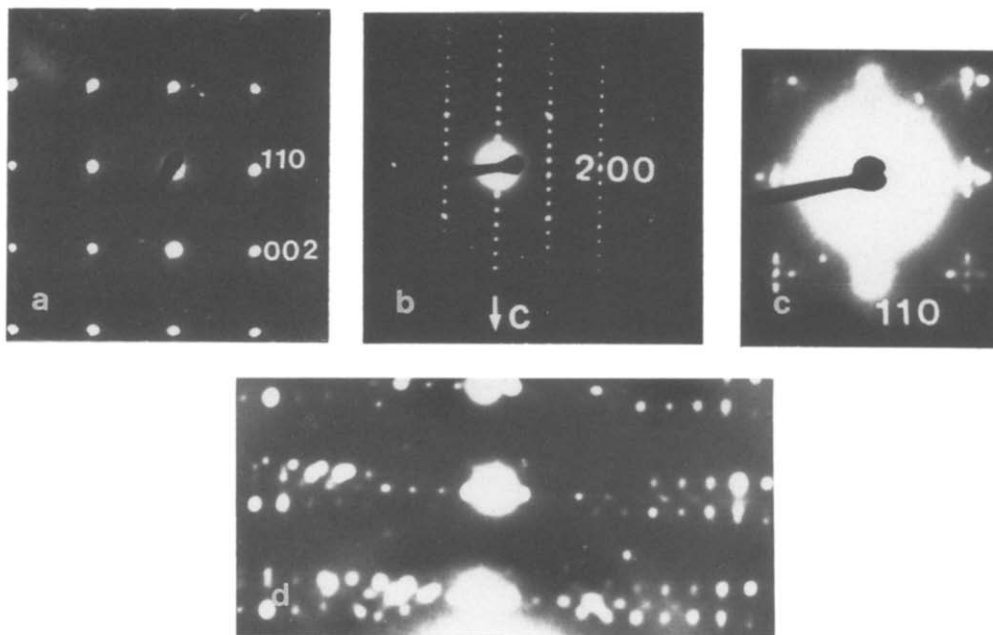
FIG. 22. $Tl_{2.7}Ba_{1.25}PrCu_2O_8$. (a) [001] and (b) [100], well-oriented patterns; (c) [001] and (d) [100], slightly deviated patterns.

the modulation factors observed for those satellites (Fig. 23) are close to integral numbers (9, ~4 and 6). In that case the $6s^2$ lone pair of Pb(II) can also extend over an anion vacancy, so that the distortion of the layer should be weak, but may exist due to the fact that the space available for this pair is limited to the rock salt layer. Moreover the modulations of the structure will be governed by the different possibilities of ordering of Pb(II), Sr, and oxygen which can take place in the rock salt layers, as shown in one example of perfect ordering given in Fig. 24.
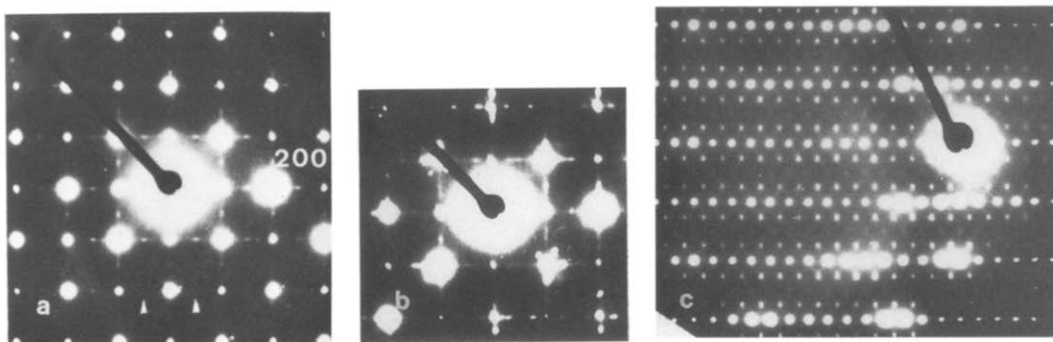
FIG. 23. E.D. [001] patterns observed for $Pb_{0.5}Sr_{2.5}Y_{0.5}Ca_{0.5}Cu_2O_7$. Weak streaks are observed along a^* and b^* axes (a); (b) satellites of second order are weak. They can be more clearly observed by a slight tilting of the crystal (c).
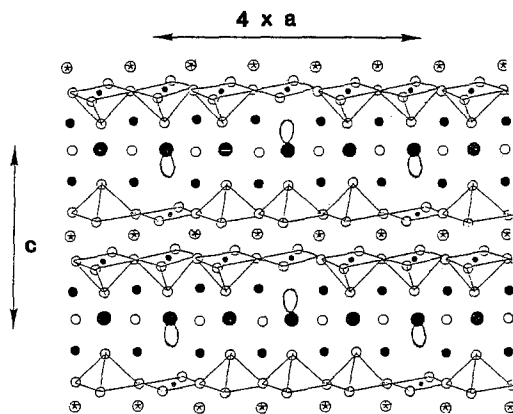
FIG. 24. $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$. Example of a perfect ordering of Pb(II) and Sr in the intermediate rock salt layers. This idealized drawing shows that $4a \times c$ superstructure can be constructed. Other models can be obtained by translation of the adjacent layers.

Concluding Remarks

The close relationships between the various layered cuprates show that a large avenue is opened to the discovery of new superconductive materials. If it is the case that the two factors which govern the superconductivity of these materials are the low dimensionality of the structure and the mixed valency of copper, it appears that the nonstoichiometry is very complex and so far not completely understood. Attention must also be drawn to the valence states of metallic elements other than copper, and specially to those of bismuth, lead, and thallium, which may also play a role in the superconducting properties of those oxides.

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