

# Description of layered structures – applications to high $T_c$ superconductors

A. Santoro

National Institute of Standards and Technology, Gaithersburg, MD 20899 (USA)

## Abstract

The layered structures of the known superconducting copper oxides can be described in terms of alternating slices having the rock salt and perovskite structure. Each slice is made up of a number of layers and each layer can be represented by specifying its chemical composition and its atomic configuration. This layer by layer representation of the crystal structures of oxide superconductors offers a convenient method for classifying and comparing to one another these important materials, and for predicting new compounds which may exhibit interesting electronic properties.

## 1. Introduction

Many important inorganic materials have crystal structures in which the atoms are arranged in layers. Familiar examples are the face-centered cubic (f.c.c.) and close-packed hexagonal (c.p.h.) stackings of identical spheres [1]. More complex cases are the structures belonging to the homologous series  $Sr_{n+1}Ti_nO_{3n+1}$  in which the layer sequences have been grouped into perovskite-type slabs interleaved with blocks containing Sr and O atoms and having the rock-salt configuration [2, 3]. Similar descriptions have also been used for materials of general formulas  $A_2BX_4$  (of which  $K_2NiF_4$  and  $La_2CuO_4$  are examples) and  $mAO \cdot nACuO_3$  ( $m$  and  $n$  are integers and  $A = Bi, Ba, Tl, \text{ etc.}$ ) [4–7].

In line with these ideas, the layered structures of the superconducting oxides, as those of compounds closely related to them, have been represented as alternating blocks with perovskite and rock-salt structures, and a symbolism has been proposed that greatly facilitates the understanding of complex structures and the building of trial models to be used in powder diffraction refinements [8]. More recently, the same compounds have been described as symmetrical combinations of (Ca, Sr)  $CuO_2$ ,  $CaTiO_3$ , and VH structural sub-units. These bi-layered building blocks are joined together through common interfaces, thus generating the known structures or predicting new ones [9–11].

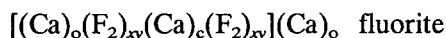
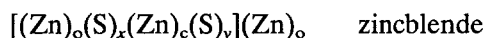
These two approaches are essentially a layer-by-layer representation of the crystal structures of the oxide superconductors. In the following sections we will outline the basic features of the method, and we will also include in our study layered compounds with atomic

arrangements other than those of perovskite and rock-salt.

## 2. Representation of layered structures

Layered structures can be described, classified, and compared to one another if we specify the chemical composition, the atomic configuration, and the sequence of the layers along a specified crystallographic direction in the unit cell. The composition may be expressed by the chemical formula corresponding to the stoichiometry of each layer, *e.g.* A,  $A_2$ , AX,  $AX_2$ , etc. The arrangement of the atoms is indicated by the coordinates of each atom referred to the axes  $x$  and  $y$  defining the mesh under consideration. Thus, if we have a layer of composition AX with atoms A at the origin of the mesh and atoms X at its center (*i.e.* shifted from the origin by the translation  $\vec{t} = \frac{1}{2}\vec{x} + \frac{1}{2}\vec{y}$ ), we may represent this configuration with the symbol  $(AX)_{oc}$  (the symbols  $(AX)_{co}$  or  $(XA)_{oc}$  then indicate that atoms A are at the center and atoms X at the origin). If the atoms A and X are located halfway along  $x$  and  $y$  respectively (*i.e.* shifted from the origin of  $\frac{1}{2}\vec{x}$  and  $\frac{1}{2}\vec{y}$ ), the symbol for the layer may be written  $(AX)_{xy}$  (the symbol  $(AX)_{yx}$  or  $(XA)_{xy}$  will then indicate that A and X are halfway along  $y$  and  $x$  respectively). For the sake of simplicity, it is generally convenient to choose the direction along which the layer sequence is defined parallel to the principal axis of each crystal system. Again for simplicity, in the case of structures based on face-centered or end-centered lattices, we will use primitive cells obtained from the centered ones by means of transformations such as  $(\frac{1}{2}, \frac{1}{2}, 0/\frac{1}{2}, -\frac{1}{2}, 0/0, 0, 1)$ .

As an example, if we apply this symbolism to the structures of zincblende, fluorite, and perovskite shown in Fig. 1, we obtain the sequences:



In these formulas the square brackets are used to indicate the layers that are contained in one unit cell of the structure.

The coordination of the atoms can be easily derived from layer sequences like those written above. For example, the atom of zinc on the layer  $(Zn)_o$  of zincblende is coordinated by two S atoms at  $x/2$  in the layer below, and by two S atoms at  $y/2$  in the layer above, thus forming a tetrahedral coordination. Similarly, the atom S of the layer  $(S)_x$  has two neighbor atoms located on the net  $(Zn)_o$  below and two located on the net  $(Zn)_c$  above, also resulting in a tetrahedral environment. With the same type of arguments it is possible to show that the atoms Ca and F in the fluorite structure have eight-fold prismatic and four-fold tetrahedral coordination, and that the atoms Ca, Ti and O of perovskite are twelve-, six-, and six-coordinated respectively.

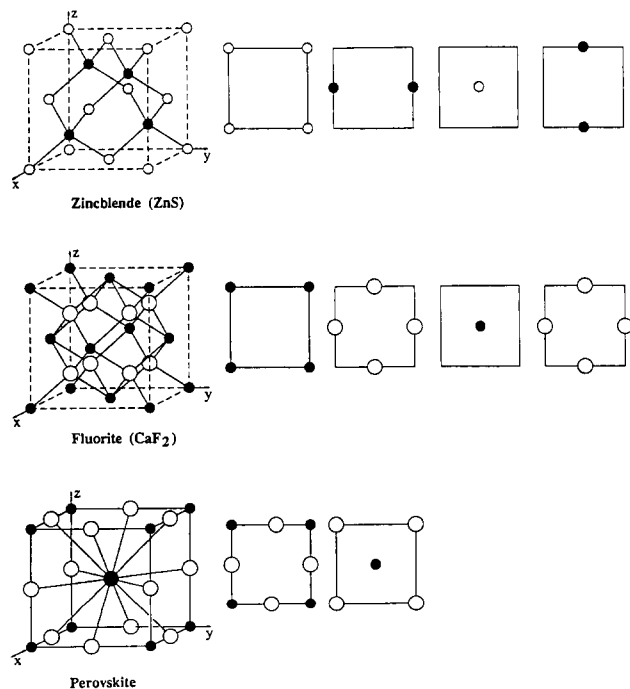
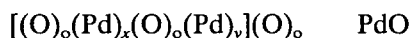
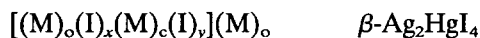
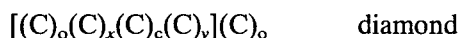
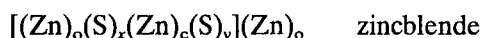


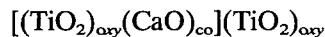
Fig. 1. Schematic representation of the unit cells of zincblende, fluorite and perovskite (left side), and atomic configuration and sequences of the layers in which the structures have been decomposed (right side). Note that the layers of zincblende and fluorite are those of primitive unit cells obtained from the corresponding centered ones by means of the transformation  $(\frac{1}{2}, \frac{1}{2}, 0/\frac{1}{2}, -\frac{1}{2}, 0/0, 0, 1)$ .

A second feature of the above sequences is that they display the symmetry, or pseudo-symmetry, of the structure in the direction of the axis perpendicular to the layers. For example, it is evident that in the structure of zincblende there can be no mirror coincident with any of the layers, but that a symmetry axis  $\bar{4}$  perpendicular to the layers may exist. On the other hand, in the case of fluorite and perovskite, mirrors coincident with  $(Ca)_c$  or  $(Ca)_o$  and with  $(CaO)_{co}$  and  $(TiO_2)_{oxy}$  are certainly possible.

Where the symbolism introduced previously is most useful, however, is in comparing structures to one another and in analyzing their geometrical relationship. Let us consider, for example, the layer sequences of zincblende, diamond, the high-temperature form of  $Ag_2HgI_4$  ( $\beta$ -form), and PdO:



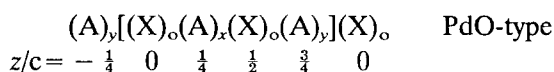
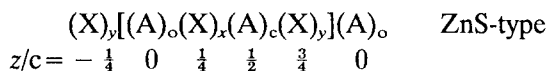
In the case of  $Ag_2HgI_4$ , the symbol M indicates an average composition  $Ag_{0.5}Hg_{0.25}\square_{0.25}$ , where  $\square$  represents a vacancy (*i.e.* the sites M are empty 25% of the time and are occupied by an atom Ag and by an atom Hg, 50% and 25% of the time respectively). We may note first that, geometrically, diamond has the same structure of zincblende, with carbon atoms replacing both zinc and sulfur. This comparison, however, does not reflect the fact that in zincblende, because of their relative size, the ions  $Zn^{2+}$  and  $S^{2-}$  are tightly packed, while the diamond structure is not the result of close packing of the atoms but of the tetrahedral spacial distribution of the carbon bonds. As we have mentioned previously, the structure of  $\beta\text{-}Ag_2HgI_4$  is disordered, but also this compound is isostructural with ZnS. Finally, the sequence of PdO is obtained from that of zincblende by replacing layers of type  $(A)_c$  with layers of type  $(A)_o$ , so that the periodicity of the sequence is entirely determined by the distribution of the Pd atoms in the unit cell. As a second example let us consider the case of perovskite and  $AlF_3$ :



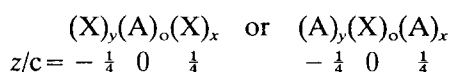
Clearly, the difference between these two structures lies in the layers sandwiched between the two  $(BX_2)_{oxy}$ -type planes (*i.e.*  $(CaO)_{co}$  in perovskite and  $(F)_o$  in  $AlF_3$ ). As a consequence of this configuration, the fluorine atoms of both the  $(AlF_2)_{oxy}$  and  $(F)_o$  layers are coordinated to two Al atoms only, while in perovskite the oxygen atoms have two Ti and four Ca neighbors. The other structural features of the two compounds

are identical, including the symmetry and the periodicity along the vertical axis perpendicular to the layers.

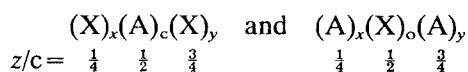
Layer sequences, being a representation of structures, can also be used to find how the coordination polyhedra around each atom are distributed in space and how they are joined together. This point may be illustrated by two simple cases. If A and X represent sites of cations and anions respectively, then sequences of zincblende- and PdO-type can be written as follows:



Let us consider the slice of layers



The sites  $(X)_y$  and  $(X)_x$  (or  $(A)_y$  and  $(A)_x$ ) form two systems of tetrahedra, one with centers at  $0,0,0$  and the other with centers at  $\frac{1}{2}, \frac{1}{2}, 0$ . Since there are no atoms at  $(A)_c$  (or  $(X)_c$ ) for  $z=0$ , but there are atoms at  $(A)_o$  (or  $(X)_o$ ), the tetrahedra of the first set are filled and those of the second are empty. In both structures, therefore, the filled tetrahedra with centers  $0,0,0$  are corner sharing and form sheets parallel to the  $xy$ -plane. Similarly, the sites  $(X)_x$  and  $(X)_y$  (and  $(A)_x$  and  $(A)_y$ ) belonging to the slices



form two systems of tetrahedra, one with centers at  $0,0,\frac{1}{2}$  and the other at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ . Only the first set is filled in the PdO-type sequence, and only the second is filled in the ZnS-type sequence. As a consequence of this different arrangement of the atoms, in zincblende the filled tetrahedra with centers at  $z=0$  and  $z=\frac{1}{2}$  are shifted one with respect to the other and share corners, while those in PdO are superposed and share edges in the  $z$ -direction.

From the above discussion it seems possible to conclude that the proposed description of layered structures may be useful (especially if used together with other geometrical approaches [12]) for understanding the atomic configuration of numerous compounds.

### 3. Compounds with the rocksalt-perovskite structure

The structures of rocksalt and perovskite are schematically represented in Fig. 2. The layer sequences corresponding to these two structural types can be written as follows:

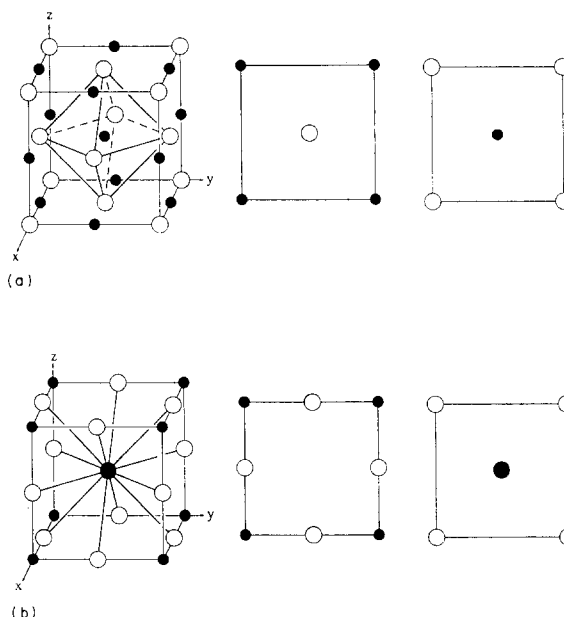
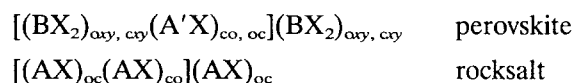
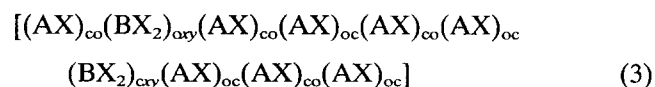
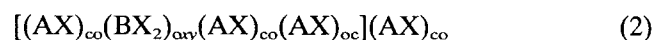
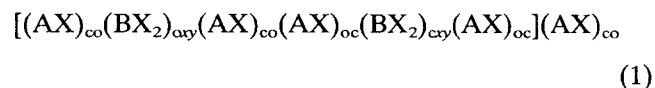


Fig. 2. Schematic representation of the unit cells of (a) rocksalt and (b) perovskite and their layer sequences. Also in the case of rocksalt the layers correspond to a unit cell obtained from the conventional face-centered cell by means of the axes transformation  $(\frac{1}{2}, \frac{1}{2}, 0/\frac{1}{2}, -\frac{1}{2}, 0/0, 0, 1)$ .



where A, A', B represent sites of cations and X sites of anions. Clearly, the layer (AX) has the same composition and the same atomic arrangement in both sequences, and it may therefore act as an interface in the formation of compounds in which slabs with the rocksalt and perovskite structure alternate along the direction of the  $z$ -axis perpendicular to the layers. The formulas written above show that before and after a layer  $(BX_2)_{oxy, cpy}$  there can only be a layer  $(AX)_{co, oc}$ , while before and after a layer  $(AX)_{co, oc}$  there can be a layer  $(BX_2)_{oxy, cpy}$  or a layer  $(AX)_{co, oc}$ . Rocksalt and perovskite slabs, therefore, can be combined in any way consistent with the scheme of Fig. 3. Examples of sequences generated in this fashion, are:



It is easy to recognize that (1) represents the structure of  $\text{LaCuO}_4$  [4], and (2) and (3) the structures of  $\text{TlBa}_2\text{CuO}_5$  [13] and  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$  or  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  [14]. The sequences (1), (2), and (3) show that structures

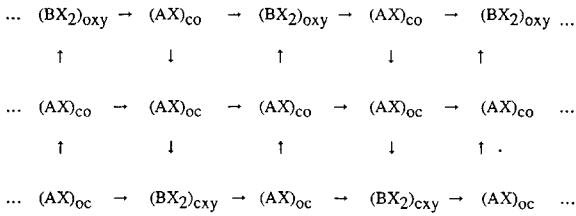
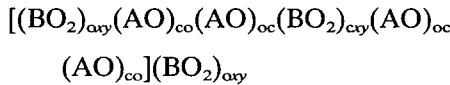


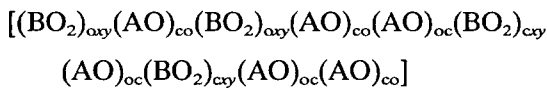
Fig. 3. Possible layer sequences of compounds with the rock-salt-perovskite structure. The first and third row represent the structure of perovskite (with the origin shifted by  $\frac{1}{2}, \frac{1}{2}, 0$ ), while the middle row correspond to the rocksalt configuration.

with an even number of rocksalt layers (AX) are made of two identical halves related to one another by a shift of the origin of  $\vec{r} = \frac{1}{2}(\vec{x} + \vec{y})$ . In the case of the structure represented by (1), for example, the two blocks related in this way are  $(BX_2)_{oxy}(AX)_{co}(AX)_{oc}$  and  $(BX_2)_{cxy}(AX)_{oc}(AX)_{co}$ . This structural feature is not present when the number of layers (AX) is odd, as in the case of sequence (2), thus resulting in a shorter periodicity along the vertical z-axis.

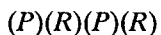
In all structures discussed so far, the perovskite blocks are made of just one layer, *i.e.*  $(BX_2)_{oxy, cxy}$ . There are cases, however, in which the perovskite configuration is more complicated. Well-known examples of structures of this type are those belonging to the homologous series  $A_{n+1}B_nO_{3n+1}$  where  $A = Sr, B = Ti$  [2, 3] or  $A = La, B = Cu$  [5]. The sequences for the structures with  $n = 1$  and  $n = 2$



and



show how the perovskite slabs increase from a monolayer  $(BO_2)_{oxy, cxy}$  for  $n=1$  to a three-layer sequence  $(BO_2)_{oxy, cxy}(AO)_{co, oc}(BO_2)_{oxy, cxy}$  for  $n=2$  and even to five- and seven-layer blocks for  $n=3$  and  $n=4$ . Since in  $A_{n+1}B_nO_{3n+1}$  the rocksalt block is always a bilayer  $(AO)_{co, oc}(AO)_{oc, co}$ , a more explicit way of writing this formula is  $\{AO\}_2\{AO\}_{n-1}\{BO_2\}_n$ . If we now allow variations also in the number of NaCl-type layers, we obtain a more general homologous series of formula  $\{AO\}_m\{AO\}_{n-1}\{BO_2\}_n$ , *i.e.*  $A_{n+m-1}B_nO_{3n+m-1}$ , which also includes the member  $ABO_3$  (perovskite) for  $n=m=1$ . The sequence of alternating blocks of perovskite and rocksalt-type may be represented with the general formula



where

$$R = m\{(AX)_{oc, co}\} \quad (4)$$

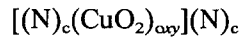
is a sequence of  $m$  layers  $(AX)_{oc, co}$  ( $m=0, 1, 2, \dots$ ) and

$$P = (BX_2)_{oxy, cxy}(n-1)\{(A'X)_{co, oc}(BX_2)_{oxy, cxy}\} \quad (5)$$

represents one layer  $(BX_2)_{oxy, cxy}$  followed by  $n-1$  bilayers  $(A'X)_{co, oc}(BX_2)_{oxy, cxy}$  ( $n=1, 2, 3, \dots$ ). In these formulas the symbol  $(A'X)$  indicates a true perovskite layer sandwiched between two  $(BX_2)$ . Finally, it is worth noting that the  $m$  layers of the rocksalt blocks may be identical to one another, as in the series  $Sr_{n+m-1}Ti_nO_{3n+m-1}$ , or they may differ in composition, as in the case of the compounds  $TlBa_2CuO_5$  and  $Tl_2Ba_2CuO_6$ .

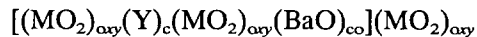
#### 4. Compounds containing slabs of defective perovskite

Many ceramic materials, some of which are well-known high- $T_c$  superconductors, have blocks of layers that may be considered to have the structure of defective perovskite. For example, the tetragonal compound  $NCuO_2$  ( $N = Ca_{0.86}Sr_{0.14}$ ) [15], has the layer sequence:



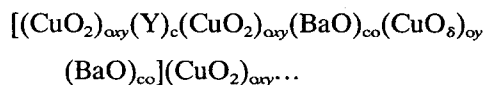
This configuration may be derived from that of perovskite by eliminating all the atoms X from the layers  $(AX)_{co}$ . As a consequence of this structural change, the atoms N have eight-fold prismatic coordination, rather than cuboctahedral as in perovskite, and the copper atoms have four-fold square-planar coordination, rather than octahedral.

The layer sequence of  $BaYM_2O_5$  ( $M = Fe_{0.5}Cu_{0.5}$ ) [16]



shows a defective layer  $(Y)_c$  similar to  $(N)_c$  present in  $NCuO_2$ . This structure, however, is more complex than the previous one since the perovskite blocks  $(MO_2)_{oxy}(Y)_c(MO_2)_{oxy}$  are now separated by  $(BaO)_{co}$  layers that may be considered as monolayers of type  $(R)$  or as part of slices of type  $(P)$ . The coordination of the Y atoms is the same as that of the N atoms in  $NCuO_2$ , but the M and Ba atoms are in five-fold pyramidal and in twelve-fold cuboctahedral coordination respectively.

Finally, the well-known 1, 2, 3 superconductor [17] is made up by the sequence:



in which two layers are defective, *i.e.*  $(Y)_c$  and  $(CuO_\delta)_{oy}$ . The first of these is the same as  $(Y)_c$  and  $(N)_c$  encountered in  $NCuO_2$  and  $BaYM_2O_5$ , and the second is part of the sequence  $(BaO)_{co}(CuO_\delta)_{oy}(BaO)_{co}$ , similar

to the sequence  $(\text{NO})_{\text{co}}(\text{CuO})_{\text{oy}}(\text{NO})_{\text{co}}$  present in  $\text{NCuO}_2$  when this structure is viewed along one of the directions perpendicular to the four-fold axis.

When defective layers of the type discussed above are taken into account, the generation of structures with rocksalt and defective and/or non-defective perovskite slabs can be accomplished by following the paths indicated by the scheme of Fig. 4.

There are many compounds in which the slabs of perovskite are defective. The most important of these, from the point of view of superconductivity, belong to a class whose general formula is  $\text{M}_n\text{N}_s\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+(r+s)}$ , where M and N are the cations in the rocksalt block

$$(R) = (\text{MO}) \dots (\text{NO}) \dots (\text{MO})$$

and Ca and Cu belong to the perovskite sequence

$$(P) = (\text{CuO}_2)_{\text{oxy, cxy}} \cdot (n-1) \{ (\text{Ca})_{\text{co, oc}} (\text{CuO}_2)_{\text{oxy, cxy}} \}$$

in which all layers of calcium are oxygen deficient. Compounds of this type form the homologous series  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  ( $\text{M} = \text{Sr}$ ,  $\text{N} = \text{Bi}$ ),  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  and  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  ( $\text{M} = \text{Ba}$ ,  $\text{N} = \text{Tl}$ ), and  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  ( $\text{M} = \text{Sr}$ ,  $\text{N} = \text{Tl}_{0.5}\text{Pb}_{0.5}$ ) [18].

In order to study the effect of the thickness of the perovskite and rocksalt slabs on the coordination of cations, let us write the sequences of the first three compounds of the homologous series  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ :

$$[(\text{BaO})_{\text{oc}}(\text{TlO})_{\text{co}}(\text{BaO})_{\text{oc}}(\text{Cu}'\text{O}_2)_{\text{cxy}}](\text{BaO})_{\text{oc}}$$

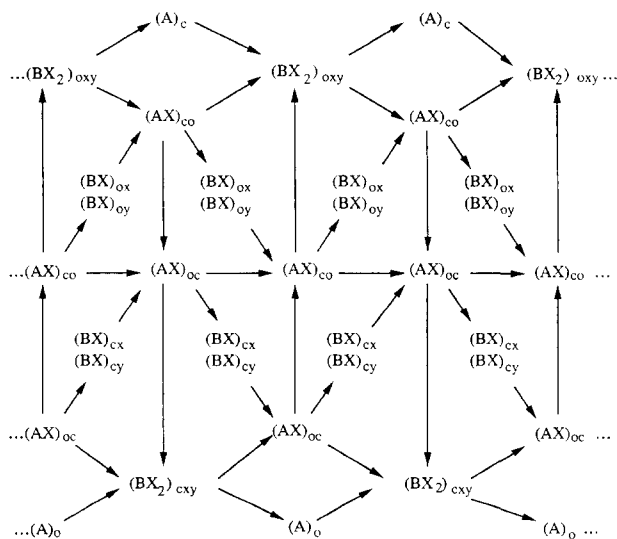


Fig. 4. Layer sequences of compounds with the rocksalt and defective and/or non-defective perovskite structure. As in the case of Fig. 3, structures can be generated by following the paths indicated by the arrows.

$$[(\text{BaO})_{\text{oc}}(\text{TlO})_{\text{co}}(\text{BaO})_{\text{oc}}(\text{Cu}''\text{O}_2)_{\text{cxy}}(\text{Ca})_{\text{o}}(\text{Cu}''\text{O}_2)_{\text{cxy}}](\text{BaO})_{\text{oc}}$$

$$[(\text{BaO})_{\text{oc}}(\text{TlO})_{\text{co}}(\text{BaO})_{\text{oc}}(\text{Cu}'''\text{O}_2)_{\text{cxy}}(\text{Ca})_{\text{o}}(\text{Cu}'''\text{O}_2)_{\text{cxy}}(\text{Ca})_{\text{o}}(\text{Cu}'''\text{O}_2)_{\text{cxy}}](\text{BaO})_{\text{oc}}$$

By using the arguments illustrated in a previous section it is easy to determine from these formulas that the coordination of  $\text{Cu}'$  ( $n=1$ ) is octahedral, that of  $\text{Cu}''$  ( $n=2, 3$ ) five-fold pyramidal, and of  $\text{Cu}'''$  ( $n=3$ ) four-fold square planar. In all cases, calcium is surrounded by an eight-fold prism of oxygen atoms belonging to the layers  $(\text{CuO}_2)_{\text{cxy}}$  below and above along the vertical axis. The Tl atoms, being on the central layer of the rocksalt block, have eight-fold octahedral coordination. The barium atoms, however, are located on a layer at the edge of the rocksalt and perovskite blocks, and are surrounded by nine oxygen atoms forming a sort of capped cuboctahedron, intermediate between the cuboctahedron typical of the perovskite structure and the octahedron typical of the rocksalt structure.

### 5. Compounds with crystallographic shear

As we have shown in the previous section, the layer sequence of the 1, 2, 3 superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$  is:

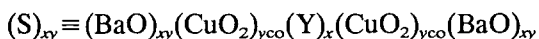
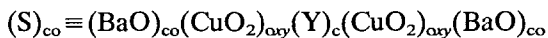
$$[(\text{CuO})_{\text{oy}}(\text{BaO})_{\text{co}}(\text{CuO}_2)_{\text{oxy}}(\text{Y})_{\text{c}}(\text{CuO}_2)_{\text{oxy}}(\text{BaO})_{\text{co}}](\text{CuO})_{\text{oy}}$$

In this compound, the defective layer  $(\text{CuO})_{\text{oy}}$  is sandwiched between two  $(\text{BaO})_{\text{co}}$  layers, thus generating the well-known chains of copper atoms in four-fold square-planar coordination propagating along the y-axis of the structure. It has been shown [19, 20] that, under certain conditions, the block  $(\text{BaO})_{\text{co}}(\text{CuO})_{\text{oy}}(\text{BaO})_{\text{co}}$  may be replaced by  $(\text{BaO})_{\text{co}}(\text{CuO})_{\text{oy}}(\text{CuO})_{\text{yo}}(\text{BaO})_{\text{xy}}$ . In other words, the defective layer  $(\text{CuO})_{\text{oy}}$  is followed by a second layer of composition  $\text{CuO}$ , shifted with respect to the first by a translation  $\frac{1}{2}\vec{y}$ , so that reasonable atomic separations are still possible. The presence of this crystallographic shear has many important consequences. First, the resulting structures are made of two identical parts with origins related by the translation  $\frac{1}{2}\vec{y}$ . For example, the sequence of the compound  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (1, 2, 4) shows clearly this feature:

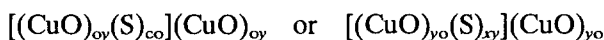
$$[(\text{CuO})_{\text{oy}}(\text{BaO})_{\text{co}}(\text{CuO}_2)_{\text{oxy}}(\text{Y})_{\text{c}}(\text{CuO}_2)_{\text{oxy}}(\text{BaO})_{\text{co}}(\text{CuO})_{\text{oy}}(\text{CuO})_{\text{yo}}(\text{BaO})_{\text{xy}}(\text{CuO}_2)_{\text{yco}}(\text{Y})_{\text{x}}(\text{CuO}_2)_{\text{yco}}(\text{BaO})_{\text{xy}}(\text{CuO})_{\text{yo}}](\text{CuO})_{\text{oy}}$$

Second, the chains of four-fold coordinated copper atoms become double chains of edge sharing squares with copper still in four-fold coordination. Finally, in this configuration each oxygen atom of the double chains is bonded to three copper atoms, rather than two as is the case in the 1, 2, 3 compound  $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$ . This feature probably explains why the oxygen stoichiometry of the bilayer  $(\text{CuO})_{oy}(\text{CuO})_{yo}$  is not variable.

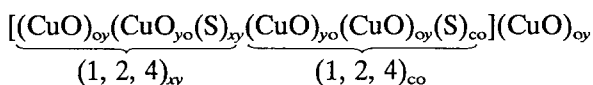
If, for the sake of simplicity, we put:



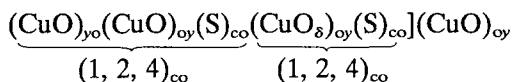
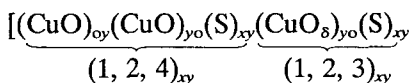
then the structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$  is represented by the sequences:



and that of the compound  $\text{YBa}_2\text{Cu}_4\text{O}_8$  by the sequence;



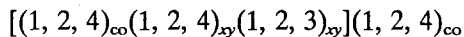
The second compound with crystallographic shear discovered so far has formula  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$  and its structure has the layer sequence:



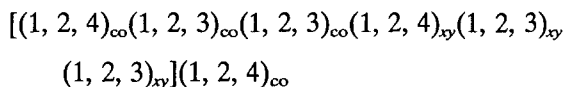
From this formula it is easy to see that the variable oxygen stoichiometry of  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$  is a result of the presence in the structure of defective layers  $(\text{CuO}_\delta)$  belonging to blocks with the configuration of the 1, 2, 3 superconductor.

On the basis of the sequences written for the two compounds with crystallographic shear characterized so far, we may conclude that these materials are made of building blocks  $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$  and  $\text{YBa}_2\text{Cu}_4\text{O}_8$  combined together in different ratios. We may therefore generalize this interpretation and say that the above compounds are members of a homologous series of formula  $m\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta} \cdot n\text{YBa}_2\text{Cu}_4\text{O}_8$ . Obviously,  $\text{YBa}_2\text{Cu}_4\text{O}_8$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$  are obtained for  $m=0$ ,  $n=1$  and  $m=1$ ,  $n=0$  respectively. The compound  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$  corresponds to  $m=1$ ,  $n=1$ . Other compounds, yet to be discovered and with more complex structures, can be predicted. For example, a compound of formula  $\text{Y}_3\text{Ba}_6\text{Cu}_{11}\text{O}_{22+\delta}$ , with  $0 \leq \delta \leq 1$ , would correspond to the composition  $m=1$ ,  $n=2$  and would have

the structure:



with an expected c-parameter of approximately 39 Å. For  $m=2$ ,  $n=1$  we would have the compound  $\text{Y}_3\text{Ba}_6\text{Cu}_{10}\text{O}_{20+\delta}$  ( $0 \leq \delta \leq 2$ ) with sequence



and an expected c-parameter of approximately 74 Å.

## References

- 1 R. C. Evans, *An Introduction to Crystal Chemistry*, Cambridge University Press, 1964, p. 80.
- 2 S. N. Ruddlesden and P. Popper, *Acta Crystallogr.*, 10 (1957) 538.
- 3 S. N. Ruddlesden and P. Popper, *Acta Crystallogr.*, 11 (1958) 54.
- 4 J. M. Longo and P. M. Raccach, *J. Solid-State Chem.*, 6 (1973) 526.
- 5 A. J. Davies and R. J. D. Tilley, *Nature*, 326 (1987) 859.
- 6 D. M. Smith, in M. F. Yan (ed.), *Ceramics Superconductors II, Research update*, American Ceramic Society, Westerville, Ohio, 1988.
- 7 A. Santoro, F. Beech, M. Marezio and R. J. Cava, *Physica, C* 156 (1988) 693.
- 8 A. Santoro, in T. A. Vanderah (ed.), *Chemistry of Superconductor Materials*, Noyes Publications, 1992, p. 190.
- 9 J. Hauck, D. Henkel and K. Mika, *Solid State Commun.*, 70 (1989) 735.
- 10 J. Hauck, D. Henkel and K. Mika, *Int. J. Modern Phys., B* 3 (1989) 1425.
- 11 J. Hauck, S. Denker, H. Hindriks, S. Ipta and K. Mika, *Z. Phys., B* 84 (1991) 31.
- 12 B. G. Hyde and S. Andersson, *Inorganic Crystal Structures*, J. Wiley & Sons (1989).
- 13 S. S. P. Parkin, V. Y. Lee, A. I. Nazzari, R. Savoy and R. Beyers, *Phys. Rev. Lett.*, 61 (1988) 750.
- 14 C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, E. M. McCarron, K. J. Morrissey, T. R. Askew, R. B. Flippin, U. Chowdhry and A. W. Sleight, *Phys. Rev., B* 38 (1988) 225.
- 15 T. Siegrist, S. M. Zahurak, D. W. Murphy and R. S. Roth, *Nature*, 334 (1988) 231.
- 16 L. Er-Rakho, C. Michel, P. Lacorre and B. Raveau, *J. Solid-St. Chem.*, 73 (1988) 531.
- 17 D. E. Cox, A. R. Moodenbaugh, J. J. Hurst and R. H. Jones, *J. Phys. Chem. Solids*, 49 (1987) 47.
- 18 S. A. Sunshine and T. A. Vanderah, in T. A. Vanderah (ed.), *Chemistry of Superconductor Materials*, Noyes Publications, 1992, p. 257.
- 19 P. Marsh, R. M. Fleming, M. L. Mandich, A. M. DeSantolo, J. Kwo, M. Hong and L. J. Martinez-Miranda, *Nature*, 334 (1988) 141.
- 20 P. Bordet, C. Chaillout, J. Chenavas, J. L. Hodeau, M. Marezio, J. Karpinski and E. Kaldis, *Nature*, 334 (1988) 569.