A Unified Description of the Crystal Structures of Copper-Containing Ceramic Superconductors

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Abstract

A simple method for describing the crystal structures of Cu-containing ceramic superconductors is reported. This provides an easy way to build up their crystal structures by joining, according to simple rules, a few small building blocks related to the perovskite unit. The crystal structures of the ceramic superconductors so far reported are described in detail using this method, which can also be applied to other kinds of mixed Cu oxides. The unified description allows the relationships between all these structures to be rationalized, and similarities and differences to be pointed out.

1. Introduction

Since the discovery by Bednorz & Müller that $La_{2-x}Ba_xCuO_4$ oxides have a superconducting transition in the 15–40 K region (Bednorz & Müller, 1986), intense experimental activity has led to the synthesis and characterization of new classes of mixed oxides, having higher critical temperatures, T_c. In fact, the well known 1:2:3-superconductors, *i.e.* $MBa_2Cu_3O_{7-x}$ where M = yttrium or lanthanide ions, have been shown to have T_c's in the range 80–95 K (Wu, Ashburn, Torng, Hor, Meng, Gao, Huang, Wang & Chu, 1987) and, more recently, Bi and Tl cuprates have been prepared with a T_c up to 125 K, the highest value so far reported (Haldar, Chen, Maheswaran, Roig-Janicki, Jaggi, Markiewicz & Giessen, 1988, and references therein; Tallon, Buckley, Gilberd, Presland, Brown, Bowden, Christian & Goguel, 1988, and references therein).

The crystal structures of a remarkable number of these mixed oxides have been determined, although some uncertainties about the content and location of oxide ions still require to be removed. As expected, the structural results have demonstrated that the knowledge of the crystal structure is a basic requirement for any model which could be proposed to explain the superconducting properties of these materials. Particularly, all the crystal structures so far determined are related in some way to that of perovskite and have a common feature, *i.e.* the presence of at least one $(CuO_2)_n$ plane, sandwiched by two planes of cations (Fig. 1). However, this feature alone is not sufficient to ensure superconductivity. In fact, the presence of copper ions having different oxidation numbers, which are generally determined by the oxide content in the unit formula, appears to be a second *conditio sine qua non* for superconductivity. In addition to the chemical analysis, accurate structural determinations, using both X-ray and neutron diffraction data, have provided useful information about this aspect. Therefore, the crystal structures of the superconducting oxides, although of significantly different stoichiometries, should have some common structural 'seeds', from which they can 'grow'.

Based on this assumption, the present work illustrates a pictorial model, which should supply a few simple keys for describing these rather complicated crystal structures in an easy way. The unified representation of the high-T_c Cu-containing superconductors may also be useful for obtaining hints for the determination of still unknown crystal structures or for suggesting new structural patterns for potential superconductors.

2. Primary and secondary building blocks

The crystal structures of the ceramic Cu-containing superconductors so far elucidated may be described by using the building blocks, derived from the perovskite unit (Fig. 2*a*), and depicted in Figs. 2(*b*)–2(*d*), or the strictly related blocks of Figs. 2(*e*)–2(*g*). Blocks of Figs. 2(*b*)–2(*d*) derive from that of the perovskite by taking off symmetrically 0·5, 1·0 and 1·5 oxide ions, respectively. Blocks of Figs. 2(*e*)–2(*g*) may be considered to be formally derived from the former blocks by substituting the copper ions of the
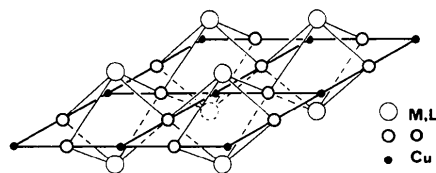

Fig. 1. Idealized representation of a $(CuO_2)_n$ plane sandwiched by two planes of cations: $M = Ba^{2+}$, $L = Tl^{3+}$, Bi^{3+}.

Table 1. *Formal charges for primary and secondary blocks*

Formula	n			
	2·5	2·0	1·5	1·0
$CuM^{II}O_n$	-1	0	$+1$	$+2$
$CuM^{III}O_n$	0	$+1$	$+2$	$+3$
$Cu_{0.5}L^{II}_{0.5}M^{II}O_n$	-1	0	$+1$	
$Cu_{0.5}L^{III}_{0.5}M^{II}O_n$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	
$Cu_{0.5}L^{II}_{0.5}M^{III}O_n$	0	$+1$	$+2$	
$Cu_{0.5}L^{III}_{0.5}M^{III}O_n$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$	

upper face with larger ions such as Tl^{3+} or Bi^{3+}, and changing positions in order to reach suitable Tl—O or Bi—O distances. Each block of Fig. 2 is characterized by its stoichiometry, derived by applying the simple crystallographic rules for counting atomic species. The formal charge is calculated from the stoichiometry and from the cation oxidation numbers, taking the oxidation number of copper as $+2$. All these blocks display a common feature, *i.e.* a $Cu_{0.5}O$ face. The general formulas are $CuMO_n$ and $Cu_{0.5}L_{0.5}MO_n$, where M (inside the block) and L (at the upper vertices of the block) are cations of oxidation number $+2$ or $+3$ and $n = 2·5$, $2·0$, $1·5$. Typical M and L are Ba^{2+} and Tl^{3+} or Bi^{3+}, respectively. The stoichiometries and the formal charges are given in Table 1. These blocks, hereinafter called *primary blocks*, will be represented by their formula followed by the formal charge in parentheses. Thus, the block of Fig. 2(*b*) will be represented as $CuM^{II}O_{2.5}(-1)$. Other blocks may be derived, which differ from primary blocks by not having the $Cu_{0.5}O$ face, as shown in Fig. 3. They, hereinafter called *secondary blocks*, may be represented in the same way as the primary blocks. Since the cation M is located in the middle of the block, the number and the positions of the oxide ions will define its coordination.

For our purposes, it is convenient to represent primary blocks by means of their two-dimensional projections. Let the Cartesian system be defined as shown in Figs. 2 and 3, with the axes coincident with the three edges of the blocks. Each block may be schematically represented by its projection on the xz plane, as indicated in the central part of both Figs. 2 and 3. It should be noted that the projections on the yz plane are the same for blocks with fourfold symmetry along z. Of the two faces perpendicular to the z axis, the low-lying face will be called d (down), the other u (up), unless they are equivalent as in the case of Fig. 2(*c*). From these projections, the stoichiometry may be derived by applying the usual rules of planar crystallography: species within the unit mesh are counted as 1, those on the sides 0·5 and those at the vertices 0·25. Furthermore, lines connecting ions represent bonds between them: full lines are bonds between ions lying in the u face (full
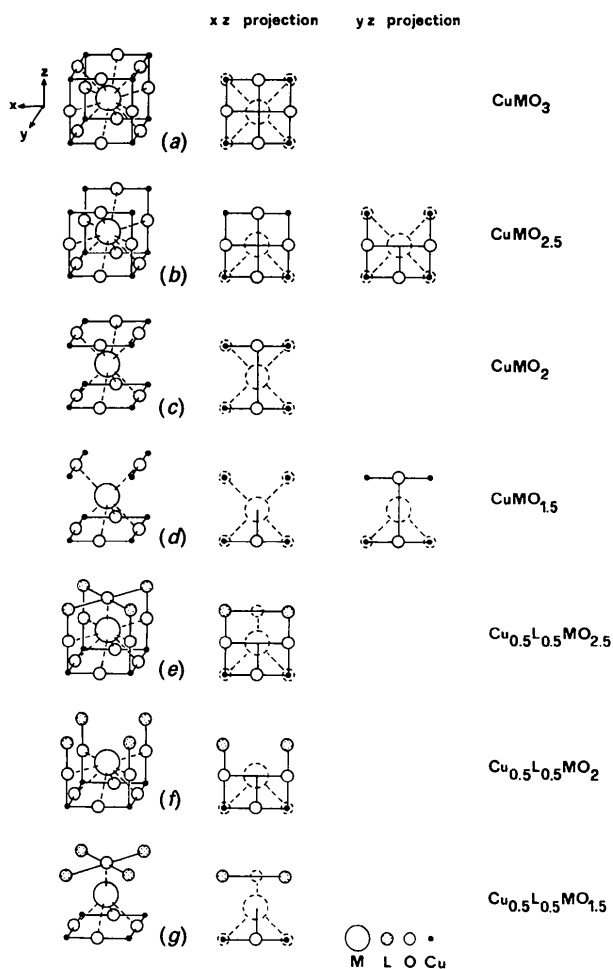

Fig. 2. Three-dimensional schemes of the primary building blocks of a given stoichiometry and their projections on the xz and yz planes. For tetragonal symmetry, only one projection is shown.
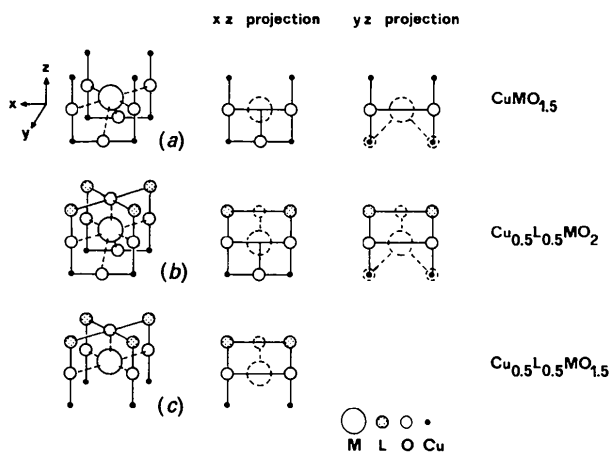

Fig. 3. Three-dimensional schemes of the secondary building blocks, together with their projections on the xz and yz planes.

circles) and broken lines bonds involving at least one lower lying ion (broken circles). The height along z of most of the blocks is defined by the distance $Cu\cdots Cu$ or $Cu\cdots L$ and depends upon the size of M and L and upon the coordination of Cu. However, it may be assumed to be approximately 4·3 Å for blocks (a), (b) and 4·8 Å for blocks (e)–(g) of Fig. 2, when L = Ba. The height of the blocks (c) and (d) is defined by the size of cation M, but it may be assumed to be approximately 3·0 Å for yttrium or lanthanides and 3·2 Å for Ca^{2+}. These values have been evaluated by using experimental data of the c axis of the unit cells described in the next sections.

3. How to use the blocks

By connecting two or more blocks along z, as described below, more complex units are built up. These in turn, by translation along x, y and z, will reproduce the crystal structure of a given superconductor. The repeat period will be defined by the length along z of this complex unit, while those along x and y will be approximately 3·8 Å, i.e. the edge length of the block in the xy plane. Since the presence of at least one 'infinite' CuO_2 plane, perpendicular to the z axis and sandwiched by two planes of cations (Fig. 1), is the only structural feature common to all these superconductors, at least one of the blocks of Fig. 2 must be present in the building unit. For this reason, they are called primary blocks. The crystal structure will be represented by the unit cell, projected onto the xz plane, and by the stoichiometry and the formal charge, derived ($vide\ infra$) from those of the constituent blocks. The possible excess of the total formal charge of the unit cell will be neutralized by a suitable number of copper ions with either +3 or +1 oxidation number.
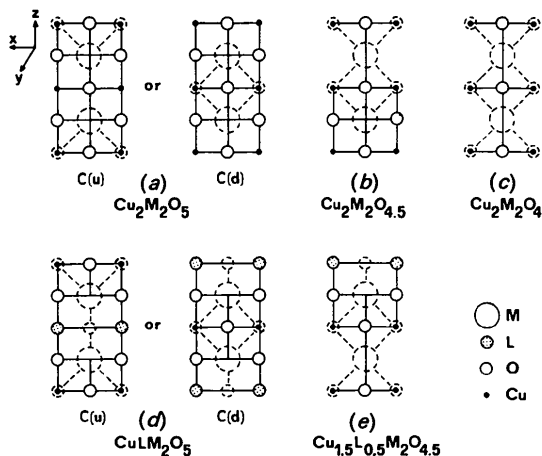

Fig. 4. Some examples of C connections, represented by projections on the xz plane. The stoichiometry of the resulting unit is also indicated.

Table 2. *Formal charges of units resulting from connections between blocks as a function of the oxidation numbers of L and M*

(a) C connections

	M^{II}	M^{III}
$Cu_2M_2O_5$	−2	0
$Cu_2M_2O_{4.5}$	−1	+1
$Cu_2M_2O_4$	0	+2
$CuL^{II}M_2O_5$	−2	0
$CuL^{III}M_2O_5$	−1	+1
$Cu_{1.5}L^{II}_{0.5}M_2O_{4.5}$	−1	+1
$Cu_{1.5}L^{III}_{0.5}M_2O_{4.5}$	−0.5	+1.5

(b) C_x or C_{xy} connections

	M^{II}_2	$M^{II}M^{III}$	M^{III}_2
$Cu_3M_2O_6$	−2	−1	0
$Cu_3M_2O_{6.5}$	−3	−2	−1
$Cu_3M_2O_7$	−4	−3	−2
$Cu_{1.5}L^{II}_{1.5}M_2O_{4.5}$	+1	+2	+3
$Cu_{1.5}L^{III}_{1.5}M_2O_{4.5}$	+2.5	+3.5	+4.5
$Cu_2L^{II}M_2O_5$	0	+1	+2
$Cu_2L^{III}M_2O_5$	+1	+2	+3
$CuL^{II}_2M_2O_6$	−2	−1	0
$CuL^{III}_2M_2O_6$	0	+1	+2
$Cu_{1.5}L^{II}_{1.5}M_2O_{6.5}$	−3	−2	−1
$Cu_{1.5}L^{III}_{1.5}M_2O_{6.5}$	−1.5	−0.5	+0.5
$Cu_2L^{II}M_2O_7$	−4	−3	−2
$Cu_2L^{III}M_2O_7$	−3	−2	−1

There are essentially two ways in which the blocks can be connected. In the first, two blocks are joined by translation along z, i.e. they share the same u or d face, normal to the z axis. The stoichiometry and the formal charge of the resulting unit are the sum of those of the two joined blocks. Analogously, the length along z of this unit will be the sum of the lengths along z of the two blocks. These connections will be indicated as C, $C(u)$ or $C(d)$ where u and d indicate the character, if any, of the joined faces. Some examples are shown in Fig. 4, together with the stoichiometries of the resulting units. Formal charges are given in Table 2. It must be stressed that the joined blocks may have different kinds of M cations.

Alternatively, two blocks can be connected to each other, binding the oxide ions on the u (or d) face of one to the cations on the u (or d) face of the other. Owing to the geometry of the joined faces, this implies that one block is displaced with respect to the other by one half of the block edge along x or along both x and y. As a consequence, the length along z of the resulting unit is equal to the sum of heights of the two blocks increased by the length of the connection, which is equal to the Cu—O or L—O distance. Its value will be assumed as 2 Å in the following calculations. The stoichiometries of the resulting units are given in Fig. 5, where (a)–(f) and (k) imply translations of one half of the block edge along x, those of (g)–(j) translations along both x and y. The corresponding formal charges are given in Table 2. These kinds of connections will be denoted by C_x and C_{xy}, respectively, followed if necessary, by the u

and d characters of the connected faces, as shown in Fig. 5. The stoichiometry and the formal charge of the resulting unit are calculated by adding to the sum of those of the two blocks, the fraction of ionic species and of formal charge of the joined faces (or segments in the two-dimensional projection). For example, the connection of two $Cu_{0.5}L_{0.5}$-$MO_{2.5}(+0.5)$ blocks is shown in Fig. 5(j). The sum of the stoichiometries and formal charges of the blocks gives $CuLM_2O_5(+1)$. The fractions for each joined segment are $L_{0.5}O_{0.5}(+0.5)$ and $Cu_{0.5}O(-1)$, respectively. By adding all these contributions, the resulting unit will be $Cu_{1.5}L_{1.5}M_2O_{6.5}(+0.5)$. The oxide-bridge formation between the two blocks requires that the upper block is translated by one half of the block edge along both x and y. The calculated stoichiometries and formal charges in some other cases are given in Fig. 5 and Table 2, respectively. Connections leading to high positive or negative charges, *i.e.*

those between blocks having formal charges of the same sign or those leading to an increase of the formal charge, should be unlikely. With these simple rules, the crystal structures of Cu-containing superconductors may be easily described, as will be shown in the next section. Additionally, new structural patterns of still unknown superconductors could be devised. For the sake of clarity, these rules are summarized as follows.

When two blocks are joined along z through a C connection:

(*a*) The resulting unit will have a stoichiometry and a formal charge which are the sum of those of the joined blocks (*rule* 1).

(*b*) The length along z of the resulting unit is the sum of those of the two blocks (*rule* 2).

When two blocks are joined along z through a C_x or C_{xy} connection:

(*c*) The stoichiometry and the formal charge of the resulting unit are calculated by adding the fraction of ionic species and of formal charges of the joined faces to the sum of those of the two blocks (*rule* 3).

(*d*) The length along z of the resulting unit is the sum of those of the two blocks increased by the height of the connection (*rule* 4).

(*e*) Connections between blocks of high formal charge of the same sign or leading to units with high formal charges are unlikely (*rule* 5).

(*f*) The repeat period along z is the c axis, while the a and b axes are coincident with the edges of the block in the xy plane (*rule* 6).

(*g*) The formal charge of the unit cell, if any, is neutralized by a suitable number of Cu^+ or Cu^{3+} ions or by a suitable adjustment of the oxide content (*rule* 7).
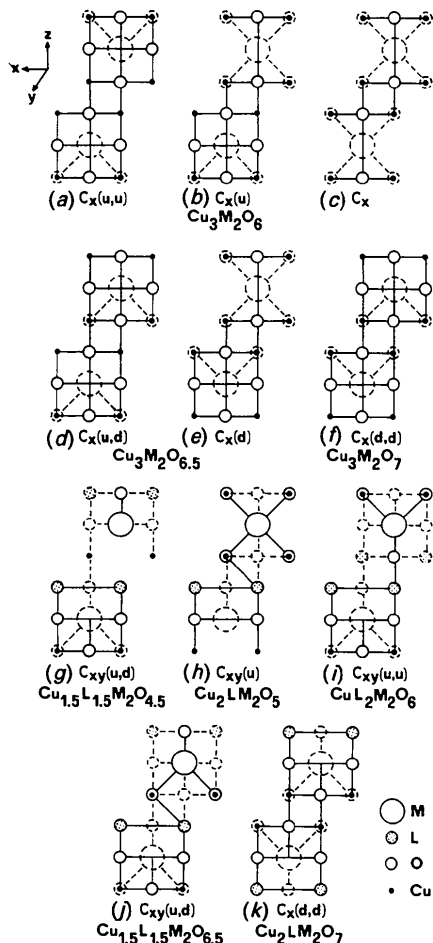

Fig. 5. Some examples of C_x and C_{xy} connections represented by projections on the xz plane. The stoichiometry of the resulting unit is also indicated.

4. Crystal structure of high-T_c Cu-containing superconductors

Following the simple criteria illustrated above, it is easy to derive the crystal structures of high-T_c Cu-containing superconductors. An equivalent way to describe the structure may be followed by using units of the kind shown in Figs. 4 and 5. This way could be more convenient for very complex structural patterns.

4.1. Rare-earth superconductors

Fig. 6(a) shows the projection on the xz plane of the unit cell of the well-known 1:2:3-superconductors. These superconductors have a general formula $LnBa_2Cu_3O_x$ ($x = 6-7$ and $Ln = Y^{3+}$ or a rare-earth ion) (Williams, Beno, Carlson, Geiser, Kao, Kini, Porter, Schultz, Thorn, Wang, Whanghbo & Evain, 1988, and references therein).

The structure is built up by joining three blocks along z: two $CuBaO_n$ blocks, with formal charge $= 0$ or -1 when $n = 2\cdot0$ or $2\cdot5$, respectively, are joined through a $C(u)$ connection and linked to one $CuLnO_2(+1)$ block through a C connection. The repeat period along z will be given by the sum of the lengths of the three blocks along z. Since each $CuBaO_n$ block is $4\cdot3$ Å long and the $CuLnO_2$ block is $3\cdot0$ Å, the c axis length should be about $11\cdot6$ Å, whereas the length of the a and b axes is approximately $3\cdot8$ Å, corresponding to the Cu—O—Cu distance. The unit-cell edges are indicated in Fig. 6(a). Here and in other figures, the unit-cell parameters are those used for the crystal structure determination. For $n = 2\cdot5$, the typical superconducting orthorhombic form $YBa_2Cu_3O_7$ is obtained, while $n = 2$ corresponds to the tetragonal non-superconducting form $YBa_2Cu_3O_6$ derived from the former, leaving out the oxide ions between each pair of Ba ions (Fig. 6a). It should be stressed that the formal charges for the unit cells of these two limiting forms are -1 and $+1$, respectively (Table 3).
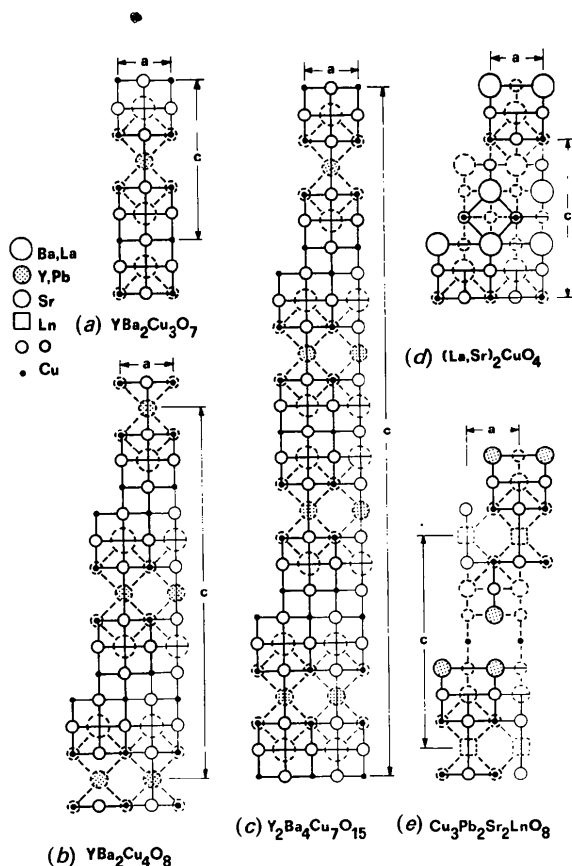

Fig. 6. Crystal structures of lanthanide-ion-containing superconductors represented in the xz plane. Heavy lines depict the blocks and connections involved in the building process. Thin lines represent blocks used to complete the unit cell, whose a and c edges are also specified.

Table 3. *Unit-cell contents, formal charges (fc) and calculated and experimental values of c axes (Å) for Cu-containing superconductors*

Content	fc/unit cell	fc/Cu ion	c(calc.)	c(exp.)
$YBa_2Cu_3O_6$	$+1$	$+\frac{1}{3}$	$11\cdot6$	$11\cdot70$
$YBa_2Cu_3O_7$	-1	$-\frac{1}{3}$	$11\cdot6$	$11\cdot85$
$Y_2Ba_4Cu_8O_{16}$	-2	$-\frac{1}{4}$	$27\cdot2$	$27\cdot24$
$Y_4Ba_8Cu_{14}O_{30}$	-4	$-\frac{2}{7}$	$50\cdot4$	$50\cdot26$
$(La,Sr)_4Cu_2O_8$	0^a	0	$13\cdot6$	$13\cdot225$
$Cu_3Pb_2Sr_2LnO_8$	$+1$	$+\frac{1}{3}$	$16\cdot6$	$15\cdot817$
$Tl_4Ba_4Cu_2O_{12}$	0	0	$23\cdot2$	$23\cdot24$
$Tl_4Ba_4Ca_2Cu_4O_{16}$	0	0	$29\cdot4$	$29\cdot32$
$Tl_4Ba_4Ca_4Cu_6O_{20}$	0	0	$35\cdot6$	$35\cdot88$
$TlBa_2CuO_5$	-1	-1	$9\cdot6$	$9\cdot002^b$
$TlBa_2CaCu_2O_7$	-1	$-\frac{1}{2}$	$12\cdot7$	$12\cdot74$
$TlBa_2Ca_2Cu_3O_9$	-1	$-\frac{1}{3}$	$15\cdot8$	$15\cdot87$
$TlBa_2Ca_3Cu_4O_{11}$	-1	$-\frac{1}{4}$	$18\cdot9$	$19\cdot01$

Notes: (a) $Sr = La$, (b) experimental value for $TlSr_2CuO_5$.

The crystal structure of a new superconductor of formula $YBa_2Cu_4O_8$ (Marsh, Fleming, Mandich, De Santoro, Kwo, Hong & Martinez-Miranda, 1988) is represented in the usual way in Fig. 6(b). The basic unit may be considered as built up of two $CuBaO_{2\cdot5}(-1)$ blocks, joined by means of a $C_x(u,u)$ connection, to form the unit $Cu_3Ba_2O_6(-2)$, which is further on connected to a $CuYO_2(+1)$ block by a C connection to give $YBa_2Cu_4O_8(-1)$.

Following rules 2 and 4, the c axis is approximately given by the sum of four blocks of $4\cdot3$ Å, two of 3 Å and two connections of about 2 Å for a total of $27\cdot2$ Å, in very good agreement with the experiment value of $27\cdot24$ Å. The a and b axis lengths are $3\cdot8$ Å each. The unit cell is shown in Fig. 6(b) and its content is $Y_2Ba_4Cu_8O_{16}(-2)$. Owing to the symmetry of the primary blocks and of the C_x connection, the unit cell must be orthorhombic.

The crystal structure of the superconductor $Y_2Ba_4Cu_7O_{14+x}$ (Bordet, Chaillout, Chenavas, Hodeau, Marezio, Karpinski & Kaldis, 1988) is represented in Fig. 6(c) for $x = 1$ and is the most complicated structure so far reported. The crystal structure may be built up by joining two unit cells of Fig. 6(a) through a $C_x(u,u)$ connection for a resulting formula $Y_2Ba_4Cu_7O_{15}(-2)$. The latter in turn, are joined through a C connection to give the unit period along z for a unit-cell content of $Y_4Ba_8Cu_{14}O_{30}(-4)$. Alternatively, this crystal structure may be described in terms of the basic units of Figs. 6(a) and 6(b). The c axis corresponds to the sum of eight blocks of $4\cdot3$ Å, four blocks of 3 Å and two connections of 2 Å, for a total of $50\cdot4$ Å, comparable with the experimental value of $50\cdot29$ Å, whereas the a and b axes are about $3\cdot8$ Å. The unit cell is shown in Fig. 6(c) and it belongs to the orthorhombic system

owing to the symmetry of the blocks and connections involved.

The crystal structure of the first ceramic superconductor, $(La,Sr)_2CuO_4$, represented in Fig. 6(d) (Onoda, Shamoto, Sato & Hosoya, 1987), may be considered as built up by blocks $Cu_{0.5}(La,Sr)_{0.5}$-$(La,Sr)O_{2.5}$ (Fig. 2e, $M = L$), joined through $C_{xy}(u,d)$ connections. The repeat period along z is reached every two units and two connections. Each block has a stoichiometry $Cu_{0.5}(La,Sr)_{1.5}O_{2.5}$ and each connection gives an extra ion content of $Cu_{0.5}(La,Sr)_{0.5}O_{1.5}$. Thus, the unit-cell content is $(La,Sr)_4Cu_2O_8$, with zero formal charge when $Sr = La$. The c axis has a length which approximately corresponds to the sum of the lengths of two blocks of 4·8 Å, and two connections of 2·0 Å, for a total of 13·6 Å, against the experimental value of 13·225 Å. The difference could be attributed to the use of a too high value for the block $Cu_{0.5}(Sr,La)_{1.5}O_{2.5}$, since both La^{3+} and Sr^{2+} ions are smaller than Ba^{2+}. The unit cell is displayed in Fig. 6(d).

The structure of superconductors of ideal formula $Cu_3Pb_2Sr_2LnO_8$, (Ln = lanthanide ions), has been recently reported (Cava, Batlogg, Krajewski, Rupp, Schneemeyer, Siegrist, Van Dover, Marsh, Peck, Gallangher, Glarum, Marshall, Farrow, Waszczak, Hull & Trevor, 1988). The crystal structure is built up by joining the primary block $Cu_{0.5}Pb_{0.5}$-$SrO_{2.5}(-1)$ and the secondary block $Cu_{0.5}Sr_{0.5}$-$PbO_{1.5}(+1)$ (Fig. 3c), through a $C_{xy}(u,d)$ connection. The latter unit is then joined to a $CuLnO_2(+1)$ block, through a C_{xy} connection. The total unit-cell content is $Cu_3Pb_2Sr_2LnO_8(+1)$. The c axis is obtained by summing up two blocks of approximately 4·8 Å, one of 3·0 Å and two connections of about 2·0 Å, giving a length of 16·6 Å, which is to be compared with the experimental value of 15·817 Å for the mixed oxide of formula $Cu_3Pb_2Sr_{2.24}$-$Nd_{0.76}O_{8+x}$. The difference between calculated and observed c values is essentially ascribable to the smaller sizes of Pb^{2+} and Sr^{2+} with respect to that of Ba^{2+}. The derived unit cell corresponds to the tetragonal primitive cell, which gives an equally good description to that given by the $Cmmm$ cell derived from the X-ray powder spectrum (Cava et al., 1988).

4.2. Tl- and Bi-containing superconductors

The ceramic superconductors with the highest T_c so far reported belong to two series of cuprates containing thallium, and to one series containing bismuth. The ideal general formulas of the two Tl series are $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ with $n = 1$, 2, 3 (Torardi, Subramanian, Calabrese, Gopalakrishnan, Morrissey, Askew, Flippen, Chowdhry & Sleight, 1988, and references therein) and $TlBa_2Ca_{n-1}$-Cu_nO_{2n+3} ($n = 1$, 2, 3, 4) (Haldar, Chen et al., 1988).

The crystal structures of the three cuprates of the first series are represented in Fig. 7. The mixed oxide $Tl_2Ba_2CuO_6$ (Fig. 7a) is built up by two primary blocks $Cu_{0.5}Tl_{0.5}BaO_{2.5}(-0.5)$ (Fig. 2e) joined through a $C(d)$ connection along z to give $CuTl$-$Ba_2O_5(-1)$ units. These units are connected through C_{xy} connections, until a repeat period is reached, after two units and two connections. Thus, applying rules 3 and 4, the total content of the unit cell is the sum of the two units content, $Cu_2Tl_2Ba_4O_{10}(-2)$, and of the contribution of the two C_{xy} connections, $Tl_2O_2(+2)$, i.e. $Cu_2Tl_4Ba_4O_{12}(0)$, which corresponds to the formula $Tl_2Ba_2CuO_6(0)$. The length of the c axis will be obtained by summing up four blocks of 4·8 Å and two connections of 2·0 Å, i.e. 23·2 Å, which compares well with the experimental value of 23·24 Å. The crystal structure of $Tl_2Ba_2CaCu_2O_8$ is shown in Fig. 7(b). The basic unit can be built up by joining the three primary blocks, $Cu_{0.5}Tl_{0.5}$-$BaO_{2.5}(-0.5)$, $CuCaO_2(0)$ and $Cu_{0.5}Tl_{0.5}$-$BaO_{2.5}(-0.5)$, in sequence, through two C connections to obtain $Cu_2TlBa_2CaO_7(-1)$. These units are joined through a C_{xy} connection to reach the repeat period after two units and two connections. Performing the usual calculations, the unit-cell content is $Cu_4Tl_4Ba_4Ca_2O_{16}(0)$ corresponding to two formula units $Tl_2Ba_2CaCu_2O_8(0)$. The length of c corresponds to the sum of those of four blocks of 4·8 Å, two of 3·1 Å and two connections of 2·0 Å, i.e. 29·4 Å, closely comparable with the experimental value of 29·32 Å. Finally, the structure of Tl_2Ba_2-$Ca_2Cu_3O_{10}$ (Fig. 7c) is built up by basic units connected in the same way as in the previous cuprates. This unit is built up by joining one $Cu_{0.5}Tl_{0.5}$-$BaO_{2.5}(-0.5)$, two $CuCaO_2(0)$ and one $Cu_{0.5}Tl_{0.5}$-$BaO_{2.5}(-0.5)$ blocks, through C connections. These units are then connected to each other through C_{xy} connections. The length of the c axis is 35·6 Å, calculated by adding the length of four blocks of 4·8 Å, four blocks of 3·1 Å and two connections of 2·0 Å, in good agreement with the experimental value of 35·88 Å. As stated at the beginning of the previous section, the crystal structure may also be described as the result of joining through C connections the two $Cu_2Ca_2O_4$ (Fig. 4c) and $CuTl_2Ba_2O_6$ (Fig. 5i) units.

All three crystal structures of Fig. 7 belong to the tetragonal system with an a axis of approximately 3·8 Å. It should be noted that the oxide contents in the above formulas require that all copper ions have a charge of +2. However, the presence of a certain number of Cu^{3+} or Cu^+ ions may be due to an excess (or defect) of oxide ions, or a deficiency of Tl cations. From the structural point of view, looking at the structures of Fig. 7 and at the corresponding stoichiometries, it is difficult to suggest where the oxide excess should be structurally located, especially

for $Tl_2Ba_2CuO_6$. On the other hand, the single-crystal structure analyses of the three compounds have always shown a relatively high thermal factor for Tl, which could mean an occupancy for this cation of less than 1.

The crystal structures of the cuprates of the other series, $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$, are shown in Fig. 8 in the usual way. All of them can be easily described as built up by joining two $Cu_{0.5}Tl_{0.5}BaO_{2.5}(-0.5)$ blocks along z, through a $C(u)$ or $C(d)$ connection. When $n = 1$ (Fig. 8a) we get a unit cell, stoichiometry and formal charge of $TlBa_2CuO_5(-1)$. The length of c is 9.6 Å which is not too far from the experimental value of 9.002 Å found for a $(Tl_{0.75}Bi_{0.25})Sr_2CuO_{4.5+x}$ phase (Haldar, Roig-Janicki, Sridhar & Giessen, 1988). As noted in other cases, the presence of Sr^{2+} instead of Ba^{2+} ions could explain the smaller experimental value. For $n = 2$, 3 and 4, the crystal structures may be considered as built up by a $Cu_{0.5}Tl_{0.5}BaO_{2.5}(-0.5)$ block followed by $n-1$ $CuCaO_2(0)$ blocks and another $Cu_{0.5}Tl_{0.5}$-$BaO_{2.5}(-0.5)$ block, all joined through C connections. The resulting formulas and formal charges per unit cell are $TlBa_2CaCu_2O_7(-1)$, $TlBa_2Ca_2$-$Cu_3O_9(-1)$ and $TlBa_2Ca_3Cu_4O_{11}(-1)$. The length of c is given by the formula $c = 2 \times 4.8 + (n-1) \times 3.1$, which leads to the values of 12.7 ($n = 2$), 15.8 ($n = 3$) and 18.9 Å ($n = 4$), in good agreement with the experimental values of 12.74, 15.87 and 19.01 Å, respectively (Haldar, Chen et al., 1988). The negative formal charge in the above formula unit should be neutralized by a certain amount of Cu^{3+} and/or a decrease in the oxide content. All the unit cells
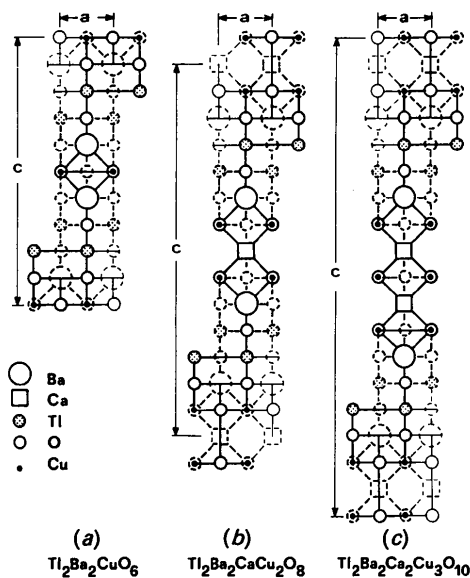
belong to the tetragonal system. The crystal structures of the Bi series, $Bi_2Sr_3Ca_{n-1}Cu_nO_{2n+4}$, with $n = 1$, 2 and 3, are very similar to those of the analogous Tl series, although some distortions impose a loss of the tetragonal symmetry (Tallon et al., 1988; von Schnering, Walz, Schwarz, Becker, Hartweg, Popp, Hettich, Müller & Kämpf, 1988).

5. Other mixed oxides

All the above structures, at least for the ideal composition, have been built up essentially by using primary blocks. However, secondary blocks could also be utilized and by using one of them, shown in Fig. 3(b), it is possible to describe the crystal structure of the mixed copper oxides with no superconducting behaviour, such as Ca_2CuO_3. In fact, two $Cu_{0.5}Ca_{0.5}CaO_2$ are joined by a $C_{xy}(u,d)$ connection (Fig. 9a). The repeat period along z, after two blocks of 4.3 Å (value derived from that of 4.8 Å for the block $Cu_{0.5}Ba_{0.5}BaO_2$, taking into account the difference in ionic radii between Ba^{2+} and Ca^{2+}) and two connections of 2 Å, is 12.6 Å, while the a and b axes of the orthorhombic unit cell are approximately equal and slightly shorter than 3.8 Å, respectively (Fig. 9). The unit-cell content is $Ca_2CuO_3(0)$ and the experimental unit-cell parameters are $a = 3.78$, $b = 3.26$ and $c = 12.24$ Å (Teske & Müller-Buschbaum, 1970). Since the crystal structure is built up solely by using a secondary block, only $(CuO)_n$ ribbons, parallel to the xz plane, are present. It should be stressed that this structure is very similar to that of $(La,Sr)_2CuO_4$ (Fig. 6d), which is built up in the same way by using the primary block $(La,Sr)_{0.5}Cu_{0.5}$-$(La,Sr)O_{2.5}$. In fact, all the oxide ions located between pairs of Cu ions along y in the latter structure are lacking in the former and cannot ensure the formation of a $(CuO_2)_n$ plane. Analogously, the crystal structure of $(Sr,Ca)CuO_2$ (Fig. 9b) is built up
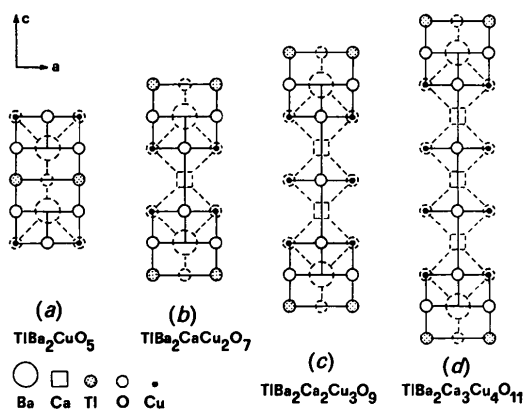

O Ba
□ Ca
⊙ Tl
O O
• Cu

(a)
$Tl_2Ba_2CuO_6$

(b)
$Tl_2Ba_2CaCu_2O_8$

(c)
$Tl_2Ba_2Ca_2Cu_3O_{10}$

Fig. 7. Crystal structures and unit cells of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ superconductors, projected on the xz plane and represented as specified in Fig. 6.

O □ ⊙ o •
Ba Ca Tl O Cu

(a)
$TlBa_2CuO_5$

(b)
$TlBa_2CaCu_2O_7$

(c)
$TlBa_2Ca_2Cu_3O_9$

(d)
$TlBa_2Ca_3Cu_4O_{11}$

Fig. 8. Unit cells of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ superconductors projected on the xz plane. The a and c directions are also shown.

from the primary block of Fig. 2(c) by simple trans-
lation along the three axes (Siegrist, Zahurak,
Murphy & Roth, 1988). The resulting crystal struc-
ture does have $(CuO_2)_n$ planes. However, since all the
Cu ions have the same oxidation number, the
cuprate cannot exhibit superconductivity.

6. Concluding remarks

The present scheme shows how all the known crystal
structures of Cu-containing superconductors are
strictly related, being based on simple connections of
a few building blocks derived from the perovskite
unit. Therefore, it represents an easy way to describe
these crystal structures and their relationships.
Furthermore, the scheme may be of help in
determining an approximate crystal structure, once
cell parameters and composition of new supercon-
ductors of this kind are known, but before single
crystals are available. Analogously, the present
scheme may be useful in obtaining tentative unit-cell
parameters from the known composition. The
agreement between the lengths of the c axis, calcu-
lated on the basis of approximate values of blocks
and connections, and the experimental values is quite
good as shown in Table 3. When the number of
structural data increases, it will be possible to derive
more accurate values for the height along z of blocks
and connections.

The formal charges per unit cell and per copper
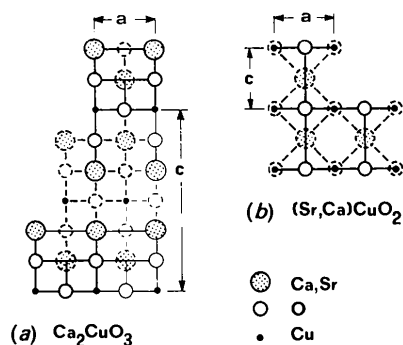ion are given in Table 3. Generally, these values are
negative, with two exceptions: in $YBa_2Cu_3O_6$ which
is not a superconductor and in $Cu_3Pb_2Sr_2LnO_8$
which is a superconductor. For the latter cases it
must be thought that there is a fraction of Cu^+,
namely 1/3, while in the others there should be a
fraction of Cu^{3+}. The formal charge of the series
$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ has been discussed in the pre-
vious section. However, it must be stressed that the
formal charges are a function of the oxide content
which, in many cases, has not yet been well estab-
lished.

Fig. 9. Crystal structures and unit cells of some non-superconduc-
ting cuprates projected on the xz plane and represented as
specified in Fig. 6.

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