Structural Chemistry and the Local Charge Picture of Copper Oxide Superconductors

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The crystal structures of the known copper oxide superconductors are described, with particular emphasis on the manner in which they fall into structural families. The local charge picture, a framework for understanding the influence of chemical composition, stoichiometry, and doping on the electrical properties of complex structures, is also described.

THE DISCOVERY OF HIGH-TEMPERATURE SUPERCONDUCTIVITY in oxides based on copper and rare and alkaline earths at first caught the solid-state physics and materials science communities completely by surprise (*1*). Since the earliest 30 to 40 K superconductors based on $La_{2-x}(Ca,Sr,Ba)_xCuO_4$, many new superconducting copper oxides have been discovered, with ever increasing chemical and structural complexity. The current record (*2, 3*) transition temperature (T_c) of 120 K is held by $Tl_2Ba_2Ca_2Cu_3O_{10}$, a material whose processing requires the stoichiometric control of five elements, each with considerably different chemical characteristics.

Enough is currently known about the copper oxide–based superconductors that certain structural, chemical, and electronic generalizations can be made that apply simply to even the most complex known materials. These are (i) the superconductivity occurs within two-dimensional copper-oxygen arrays based on the joining of CuO_4 squares at their oxygen corners to form infinite CuO_2 planes; (ii) the superconducting CuO_2 planes are separated by charge reservoir layers that act to control the charge on the superconducting planes (through chemical doping) either through the transfer of holes or electrons (*4*), to some optimal concentration dependent in detail on the overall structure; (iii) the electronic band at the Fermi level is one which is highly hybridized due to the similarity in energy between copper 3d and oxygen 2p states (*5*); and (iv) the superconductivity occurs in all cases at the doping level where an originally antiferromagnetic insulator loses its local moments and becomes metallic.

With T_c's now having reached 120 K, very few are arguing in favor of conventional electron-phonon coupling for the microscopic pairing mechanism in copper-based superconductors, especially in light of the surprisingly small changes in T_c with oxygen isotope substitution (*6*). Many theorists have been drawn to the apparent relationship between antiferromagnetism and superconductivity and proposed magnetic origins for the pairing (*7*). Others propose electronic origins for the pairing (*8*). There is as yet no consensus on this issue.

No doubt the proliferation of copper-oxide superconductors looks like alphabet soup to the non–crystal chemist. All the compounds, however, belong to a handful of structural families. Once the basic building principles of these families is laid out, their relationships are easily seen, and their apparent complexity clarified. The chemical complexity arises due to the need to satisfy geometrical and electrical charge requirements necessary for each particular member of a family. It has been pointed out that all the known superconductors can actually be derived by stacking different amounts and sequences of rock salt and perovskite-like layers of metals and oxygen (*9–11*).

The first part of this article describes the crystal structures of the copper oxide superconductors, arranged in their structural families. In the second part, a somewhat hypothetical picture by which the common features of all the structures can be understood is described. This local charge picture, which my collaborators and I believe is most succinctly illustrated by detailed consideration of oxygen-deficient $Ba_2YCu_3O_{7-x}$, is important in understanding the electronic doping mechanism of the copper oxide planes in the structurally more complex materials.

Structural Families

Copper-based oxides form easily under standard ceramic processing conditions and therefore many compounds are known. The size of the Cu^{2+} ion in oxides is such that when in combination with alkaline and rare earth ions, the perovskite family of compounds and their derivatives are easily accessible. Critical also to the ease of compound formation are the variable formal valence of copper (between +1 and +3), and the variety of coordination polyhedra available for copper and oxygen. Unlike many transition metal oxides, the various formal valences of copper are easily accessible under straightforward temperature and oxygen partial pressure conditions: variability between "+2.5" and +1 is possible at temperatures between 500° and 1200°C in oxygen partial pressures attainable by mixing bottled O_2 and N_2 gas. Copper oxygen coordination can be linear (twofold) for Cu +1, and square planar (fourfold), pyramidal (fivefold) and octahedral (sixfold) for valence states of +2 and higher. The "octahedra" for Cu +2 are Jahn-Teller distorted. This variability in possible coordination polyhedra increases the variety of geometries that Cu-based compounds can have, but has also turned out to be critical in allowing the accommodation of nonideal oxygen stoichiometries. Finally, the coordination requirements of copper ions in the formal valence range of interest, between 2+ and 3+, are similar enough that oxidation/reduction can occur within a single basic coordination polyhedron without serious structural rearrangement.

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A good starting point to begin discussions of the detailed crystal structures of the copper oxide superconductors is the perovskite structure, shown in an idealized representation in Fig. 1. $LaCuO_3$, which must be prepared at high oxygen pressures, has a distorted version of this basic structure in which Cu-O-Cu bond angles are not 180° (*12*). For copper-based materials, it is best to consider the perovskite structure as made ideally of alternating CuO_2 and AO layers where A represents the large perovskite ion. The CuO_2 layers have the basic geometry of a corner shared array of square planar (CuO_4) copper oxygen polyhedra (each oxygen bonded to two coppers) with approximately 180° Cu-O-Cu bond angles. The AO layer is also comprised of square planar coordination polyhedra but is completely edge-shared such that each oxygen is bonded to four A atoms resulting in an AO stoichiometry; the A-O bond length is approximately $\sqrt{2}$ times the Cu-O bond length for successful stacking of the AO-CuO_2 arrays, in which the O from the AO layer stacks directly above the Cu of the CuO_2 layer. The stacking sequence is CuO_2-AO-CuO_2-AO-.

Often, copper prefers to be coordinated to fewer than six oxygens, and the smaller rare and alkaline earths prefer to be bonded to eight or nine oxygens, and so in copper-based oxides the ideal perovskite coordination numbers (6 for the B ion and 12 for the A ion) are not generally found. This is accommodated in the known superconducting compounds either through stacking sequence differences or the presence of ordered vacant oxygen sites in either the AO or CuO_2 layers. The compound $Ca_{0.84}Sr_{0.16}CuO_2$, for instance (*13*), is the simplest oxygen-deficient variation of the perovskite structure, with a 1:1 A to B ratio but with one-third of the oxygens missing in an ordered manner. The stacking sequence is CuO_2-A-CuO_2-A- where A = $Ca_{0.84}Sr_{0.16}$. The infinite CuO_2 planes are complete, with all oxygens missing from the A layer, resulting in fourfold Cu-O coordination and eightfold (square prismatic) A-O coordination. The stacking sequence CuO_2-A-CuO_2 is the structural kernel of all of the known superconductors with T_c's greater than 40 K, and seems empirically to be clearly indicated as a necessary (but not sufficient) structural component. With that importance in mind, it is of particular interest to note that this crystalline structure, although existing for $Ca_{0.84}Sr_{0.16}CuO_2$, does not exist for either pure end member $CaCuO_2$ or $SrCuO_2$ at ambient pressure, suggesting that its stability is very critically dependent on the size of the atomic array, with the eight coordinate radii of Ca^{2+} (1.12) and Sr^{2+} (1.25) differing by only 10%! Pure $SrCuO_2$ has recently been prepared at high pressures in this structure type (*14*).

Figure 1 illustrates the manner in which a structural family can be derived from the basic perovskite structure type. On the left, an idealized $LaCuO_3$ perovskite is shown, and on the right, La_2CuO_4, which is the host compound for the 20 to 40 K superconductors (*15*). The La_2CuO_4 structure is easily derived from that of $LaCuO_3$ by the insertion of one additional AO layer. The new stacking sequence is now (CuO_2)-(AO)-$(AO)_c$-$(CuO_2)_c$-$(AO)_c$-(AO)- where the subscript c means that these layers have been shifted by $1/2a + 1/2b$ in the plane of the layer. The (AO)-$(AO)_c$ sequence is exactly the arrangement of atoms found in NaCl, so one can consider this material as a mixture of perovskite and sodium chloride structure types. In La_2CuO_4, Cu is surrounded by six oxygens, as in the simple perovskites, but the large A atoms are only nine-coordinate with oxygen, as their neighboring layers are CuO_2 and centered AO. The principle of layer insertion is central to the formation of homologous series in oxides and is illustrated in this chemical system in the center of Fig. 1 which represents the structures of $La_2CaCu_2O_6$ and $La_2SrCu_2O_6$ (*16*). There are potentially a very large number of compounds [Ruddlesden-Popper phases (*17*)] of the type $A_{n+1}Cu_nO_{3n+1-\delta}$ for which La_2CuO_4 and $LaCuO_3$ are the end members $n = 1$ and $n = \infty$. The A ions, which may be mixed, and δ are chosen for charge balance. $La_2CaCu_2O_6$ is the $n = 2$ member of the series. The A ions are ordered such that the small Ca ion takes eight oxygen neighbors, and we have the stacking sequence: (CuO_2)-(AO)-(AO_c)-$(CuO_2)_c$-$(A')_c$-$(CuO_2)_c$-$(AO)_c$-(AO)-(CuO_2)-(A')-. The structure type that results is a mixture of that of La_2CuO_4 and that of $Ca_{0.84}Sr_{0.15}CuO_2$. This compound has not to date been successfully doped to give it metallic conductivity, but it clearly satisfies the structural criteria for high T_c superconductivity.

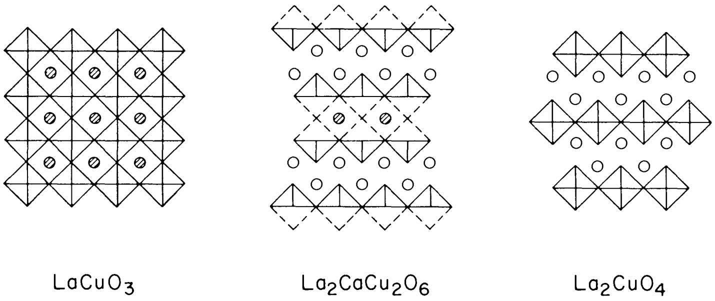


Fig. 1. Idealized crystal structures of members of the family $A_{n+1}Cu_nO_{3n+1-\delta}$. Copper-oxygen polyhedra shown as octahedra and square pyramids, rare and alkaline earths shown as clear and shaded circles (dotted lines show how square pyramids are derived from incomplete octahedra in the $La_2CaCu_2O_6$ structure type).

For the case of two A site ions per Cu, three distinct but structurally related superconducting phases are known. This family of compounds is illustrated in Fig. 2. When doped appropriately, superconductivity occurs in the temperature range of 20 to 30 K. The first member La_2CuO_4 has been described. The so-called T* phase (*18*) is formed when the A site ions are a mixture of larger rare earths which prefer nine oxygen neighbors, and smaller rare earths which prefer eight oxygen neighbors. The result is single layers of corner-shared CuO_5 pyramids, as opposed to octahedra as are found in La_2CuO_4. This structure can actually be considered as an ordered mixture of the metal oxygen layers found in La_2CuO_4 (the "T" structure) and the structure found at the 2:1 stoichiometry for the intermediate size rare earths Pr-Gd (the T′ structure). This latter structure (*19*) is also shown in Fig. 2. The rare earth oxygen layers contain only eight coordinated square prismatic rare earths, with the result being that the copper-oxygen layers are corner-shared square planar arrays only. The T′ phase is of considerable importance as it becomes an n-type superconductor when appropriately doped (*4*).

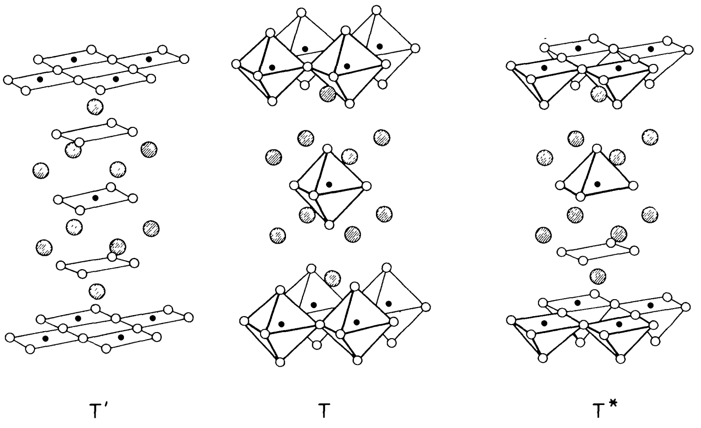


Fig. 2. Members of the family of compounds with 2A site ions per Cu. The rare earths are shown as shaded circles, the copper as small closed circles, and the oxygens as small open circles. Coordination polyhedra of the Cu are emphasized by solid lines (note Cu is 4, 6, and 5 coordinate in T′, T, and T*, respectively).

Comparing the stacking sequences of the members of this family, we have:

T: $\text{-(CuO}_2\text{)-(MO)-(MO)}_c\text{-(CuO}_2\text{)}_c\text{-(MO)}_c\text{-(MO)-}$

T*: $\text{-(CuO}_2\text{)-(M')-(O}_2\text{)-(M')}_c\text{-(CuO}_2\text{)}_c\text{-(MO)}_c\text{-(MO)-}$

T′: $\text{-(CuO}_2\text{)-(M')-(O}_2\text{)-(M')}_c\text{-(CuO}_2\text{)}_c\text{-(M')}_c\text{-(O}_2\text{)-(M')-}$

Buried in this type of description is the fact that the copper coordination in the active layer is quite different in each member of the family, being six-, five-, and four-coordinate to oxygen in the T, T*, and T′ phases, respectively. It is, surprisingly, apparently not that important for the superconductivity in this case, as all T_c's are in a similar temperature range.

After the determination of the crystal structure of the 90 K T_c compound $Ba_2YCu_3O_7$, with its infinite sheets of CuO_5 square pyramids sandwiching square planar CuO_4 chains (*20*), it was natural to attribute the factor of 2 increase in T_c (over doped La_2CuO_4) intimately to the chains, or to a combination of chains and planes. In fact after initial elation over the beauty and uniqueness of a crystal structure that combined one- and two-dimensional structural elements so remarkably, the prospects for finding wholly new superconducting compounds with similarly unique structural characteristics seemed remote: even though copper chains may be found in some compounds, and planes in others, nowhere else but in "123" did both occur together. It was really only after the determinations of the crystal structures of the Bi and Tl based cuprates that the role of the chains in $Ba_2YCu_3O_7$ could be understood. It is now clear that the chains and other secondary structural elements act as charge reservoirs which control the charge concentration on the copper-oxygen planes that are the critical structural component in superconductivity.

$Ba_2YCu_3O_7$ is the most well known member of a very interesting homologous series of compounds. Figure 3 schematically represents the presently known compounds in the series, beginning with $BaYCuFeO_5$ (*21*) which consists of infinite planes of copper/iron oxygen square pyramids stacked through sharing their apical oxygen atoms. The stacking sequence for this compound is: $\text{-Y-(Cu/Fe)O}_2\text{-BaO-(Cu/Fe)O}_2\text{-}$. The homologous series is formed by the insertion of copper-oxygen chains between the apices of the pyramids. In this sense, $Ba_2YCu_3O_7$ is the simplest member of the series containing chains, with one chain (and a BaO plane) inserted between each set of square pyramids. The stacking sequence is: $\text{-Y-CuO}_2\text{-BaO-CuO-BaO-CuO}_2\text{-}$. One way the series can be expanded is through the addition of more layers of chains sharing only corners with each other with a BaO layer accompanying each, with the formulae $Ba_{2+n}Y_2Cu_{4+n}O_{10+2n}$. Only the $n = 0$ and $n = 2$ compounds are presently known ($BaYCuFeO_5$, $Ba_2YCu_3O_7$). Another way the series can be expanded is through the addition of edge-shared "double chains" of the CuO_4 squares. These are actually variations of the first structural series derived by way of crystallographic shear. The crystallographic shear eliminates the otherwise present interleaving "A" atom-oxygen layer, such that only copper-oxygen layers are added, resulting in the ideal formulae $Ba_4Y_2Cu_{6+n}O_{14+n}$. The first three members of this series are in fact known ($n = 0, 1, 2$) and are shown in Fig. 3, the latter two (*22, 23*) having been synthesized under relatively unconventional synthetic conditions. It would in fact be surprising if members with $n > 2$ would be found as there do not seem to be any examples of simple "triple chain" copper oxides known, but we have certainly been surprised before.

From a crystal-chemical point of view, the Tl- and Bi-based copper oxides form the most straightforward homologous series of compounds, though their synthesis and characterization is certainly far from straightforward [see (*24–26*) and references therein for detailed reviews of these compounds]. These compounds advanced the field not only by their very high T_c's, but also through the fact that they made it clear that only copper-oxygen pyramidal planes are necessary for superconducting T_c's near 100 K. In addition to the classical structure/composition relations found in these materials, they display other characteristics of homologous series which make them of significant interest (and frustration) to the crystal chemist: (i) deviations from ideal stoichiometry are generally accommodated by the formation of extended and not point defects, primarily through intergrowth of different members of the series on a microscopic scale, and (ii) as the complexity (number of stacks) increases, the compounds have smaller and smaller temperature/composition regions in which they can be successfully formed.

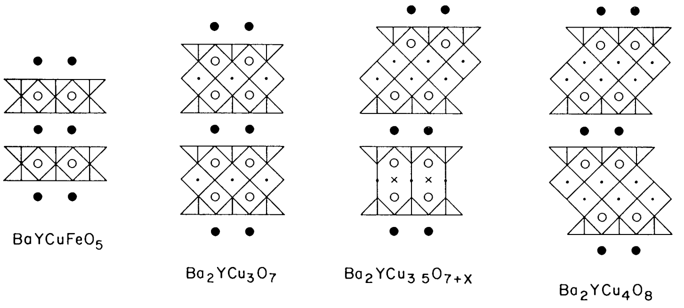
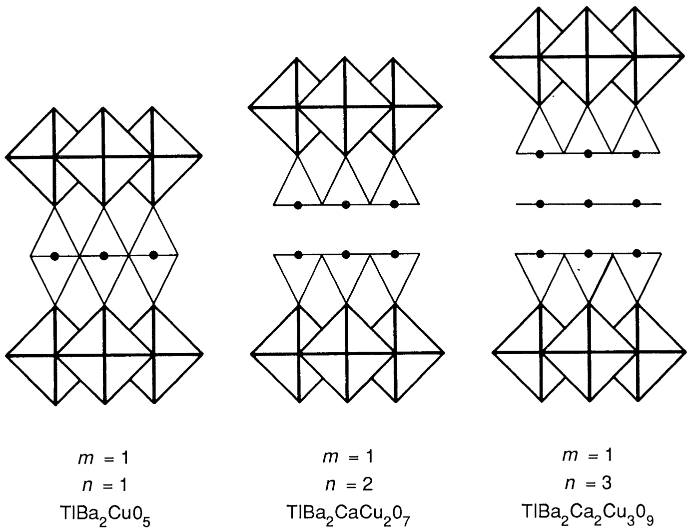

$BaYCuFeO_5$ $Ba_2YCu_3O_7$ $Ba_2YCu_{3.5}O_{7+x}$ $Ba_2YCu_4O_8$

Fig. 3. Idealized crystal structures of the Ba-Y-Cu-O family, showing Cu-O coordination polyhedra, Y (black circles), Ba (open circles), and four coordinated Cu as black dots within O diamonds. The cross indicates position where oxygen stoichiometry is variable in $Ba_2YCu_{3.5}O_{7+x}$ (and $Ba_2YCu_3O_{7-x}$).

Perhaps the most interesting crystal chemical aspect of these materials is that for those based on Tl there exist not only variable numbers of Cu-O layers but also variable numbers of Tl-O layers, which makes for the possibility of many compounds, in what is really an infinitely adaptive series. The whole series can be written as: $Tl_mBa_2Ca_{n-1}Cu_nO_{m+2n+2}$. The subscript m defines how many rock salt layers are present, and to date examples have been found for $m = 1$, and 2. The number of copper layers is remarkably variable, with $n = 1, 2, 3, 4$ presently claimed to be prepared as bulk materials. Even more remarkably, all compounds thus far synthesized in this series are claimed to be superconducting. Unfortunately, compounds based on Bi-Sr-Ca-Cu-O have proven to be much more difficult to make in anything other than the $m = 2$, $n = 1, 2$ structures. The precise metal stoichiometries of some of the Bi-Sr-Ca-Cu-O based compounds have been somewhat controversial. The problem is that Bi, Sr, and Ca could possibly substitute for each


$m = 1$, $n = 1$, $TlBa_2CuO_5$

$m = 1$, $n = 2$, $TlBa_2CaCu_2O_7$

$m = 1$, $n = 3$, $TlBa_2Ca_2Cu_3O_9$

Fig. 4. Idealized crystal structures of the $m = 1$, $n = 1$–3 members of the family $Tl_mBa_2Ca_{n-1}Cu_nO_{m+2}$. Cu shown as small black dots, TlO_6 octahedra outlined, as are Cu-O pyramids.

other in these materials. However, virtually all the phases can be prepared as pure superconducting compounds at their ideal stoichiometries, suggesting that small deviations therefrom are either insignificant or irrelevant. The $m = 2$, $n = 3$ member of the series can be synthesized in pure form most successfully by the partial substitution of Pb for some of the Bi on the NaCl type layers (*27*).

Figures 4 and 5 illustrate the structures in this family, and show the interesting manner in which they are related to each other. The $n = 1$ member contains a single copper-oxygen layer consisting of elongated octahedra sharing corners. For the $n = 2$ member, the octahedra are split into two pyramids each, with their bases separated. For $n = 3$, a square planar CuO_2 layer is inserted between the pyramids. Thus in the progression from $n = 1$ to 3, the coordination of the copper layers changes dramatically. For all $n > 2$ more CuO_2 square planar layers are added. As many have noted, for the Tl-based materials T_c increases with the number of copper layers up to $n = 3$, and then decreases for larger n. Although the ($m = 2$) $n = 4$ compound can be prepared relatively purely, compounds with higher numbers of copper layers have been observed only as intergrowths. Remarkably, such intergrowth regions with as many as seven copper-oxygen layers have been observed (*28*).

The thallium-oxygen and bismuth-oxygen layers are also interesting. The layers of edge-shared $Tl(Bi)O_6$ octahedra share their apical oxygens with the apical oxygens of the copper-oxygen pyramids or octahedra. For materials with a single edge-shared layer ($m = 1$), that layer is sandwiched between active copper layers. For materials with two edge-shared octahedral layers, those layers also share edges with each other, as shown in Fig. 5. For Bi-based materials, only the double edge-shared layers ($m = 2$) are found. The BiO_6 octahedra are strongly distorted into three short and three long bonds. There is a very prominent cleavage plane between the BiO layers. Perhaps it is the strong distortion of this Bi-O bonding that prevents the formation of the single edge-shared members for Bi-based materials. For both the Tl- and Bi-based members of this family, there occur incommensurate structural modulations. Those structural modulations for the Tl family are due to only small deviations of the atoms from their mean positions (*29*), but for the Bi members the positional distortions are large. By solution of the crystal structure of an analogous compound, $Bi_2Sr_3Fe_2O_9$, where the periodicity is commensurate, it has been established that the structural modulation is due to the periodic insertion of oxygen, resulting in approximately one in every five Bi having more than six oxygen neighbors, distorting the whole Bi-O array (*30*).

The most recent family of copper oxide superconductors to come to light (*31*) is based on the stacking of copper oxide layers with an intermediary layer which is more complex than those found in the earlier known materials. The intermediary layer is a combination of the TlO-like layers found in Tl-based compounds and the CuO_x, layers found in the 123 family of compounds. The layers are made of Pb-O and CuO_x in the sequence -PbO-CuO_x-PbO-. The Pb is in a divalent state, and, in the superconducting compounds, $x = 0$. The two known members of the family $Pb_2Sr_2(Y,Ca)Cu_3O_8$ (*31*) and $Pb_2(Sr,La)_2Cu_2O_6$ (*32*) are illustrated in Fig. 6. The homologous series has the formula $Pb_2M_2M'_{n-1}Cu_{n+1}O_{4+2n+x}$ of which only the members $n = 1$ and $n = 2$ are known. For the $n = 1$ compound, the active copper-oxygen layers consist of octahedrally coordinated copper with rare and alkaline earths in the sequence -(Sr,La)O-CuO_2-(Sr,La)O-. For the $n = 2$ compound, the active CuO layers are copper-oxygen pyramids with bases facing each other, with the layer sequence -SrO-CuO_2-(Y,Ca)-CuO_2-SrO-. Thus the active copper layers are exactly analogous to those found in the BiO- and TlO-based compounds. As for those compounds, T_c increases dramatically as n increases from 1 to 2 (the maximum T_c is 80 K). T_c might be expected to be higher for the $n = 3$ member, which would have active copper layers in the same geometry as found for the $n = 3$ TlO compounds, if it could be synthesized. The oxygen stoichiometries in these compounds are highly variable. In $Pb_2Sr_2(Y,Ca)\,Cu_3O_{8+x}$, x can be between 0 and 1.8. Importantly, the $x = 0$ compound (which has Cu^{1+} and Cu^{2+}) cannot be made superconducting through the addition of oxygen. Superconductivity can be induced only through oxidation of copper by partial substitution of Ca for Y. Oxygen addition cannot oxidize the copper

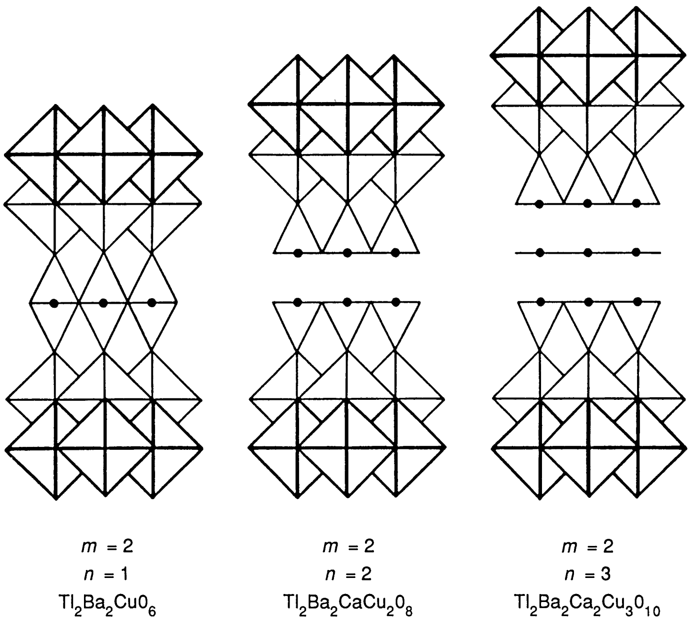


Fig. 5. Idealized crystal structures of the $m = 2$, $n = 1$–3 members of the family $Tl_mBa_2Ca_{n-1}Cu_nO_{m+2n+2}$. Cu shown as small black dots, TlO_6 octahedra outlined, as are Cu-O pyramids.

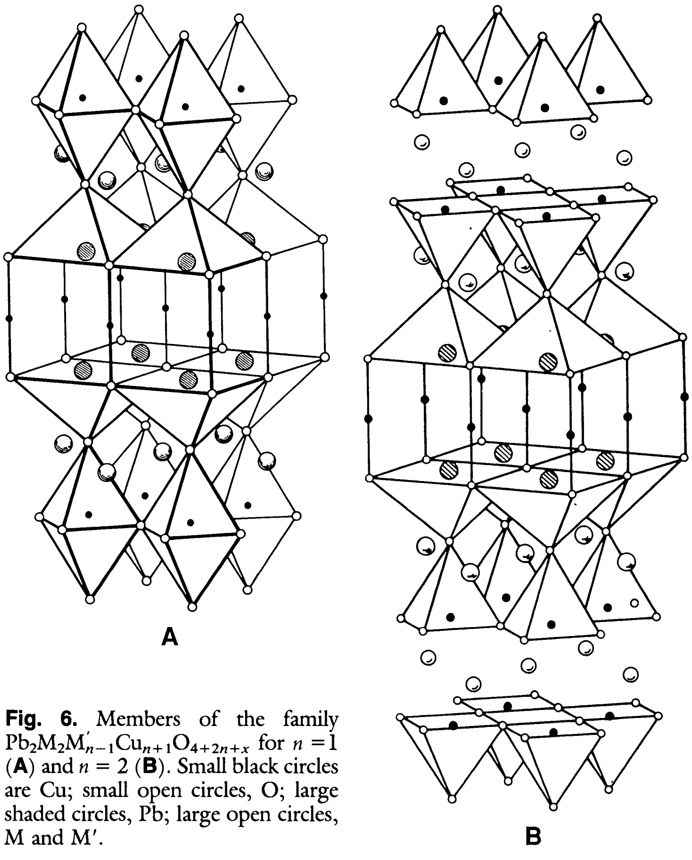


Fig. 6. Members of the family $Pb_2M_2M'_{n-1}Cu_{n+1}O_{4+2n+x}$ for $n = 1$ (**A**) and $n = 2$ (**B**). Small black circles are Cu; small open circles, O; large shaded circles, Pb; large open circles, M and M′.

because it oxidizes the divalent Pb instead. This compound is an important example of the manner in which the local charge picture can be used to understand the layered copper oxide superconductors, and will be discussed in further detail in the following.

The Local Charge Picture

For all the layered copper oxide superconductors, superconductivity is induced into a normally antiferromagnetic insulator by the addition of positive or negative charge (hole or electron doping) to a CuO_2 plane. In the p-type superconductors this corresponds to the oxidation of the Cu^{2+} in the CuO_2 plane to a formal valence between 2 and 3. In the n-type superconductors, which are known only for electron doping of the T' structure (Fig. 2), this corresponds to a reduction of the Cu^{2+} in the CuO_2 plane to a formal valence between 2 and 1. Of course the hybridization with oxygen 2p orbitals makes the formal charge different from the true charge on copper, but the formal charges present a good framework for thinking about doping levels in a quantitative way. For the simplest materials, the microscopic understanding of the manner in which chemical substitutions or non-stoichiometry dope the CuO_2 planes is not difficult, but as the materials become more complex, that doping process becomes less straightforward.

The "local charge" picture provides a basis for understanding the doping process in a wide variety of materials. It is a hypothetical picture through which my collaborators and I, and other workers in the field, attempt to categorize (and extract information from) the known copper oxide superconductors. At the center of the local charge picture is the idea that all the layered copper oxide superconductors have crystal structures that can be considered as built of electronically active CuO_x superconducting layers sandwiched between other structural layers which act as spacers, and, most importantly, as electronic charge reservoirs. The doping of the active CuO_x layers is controlled by the electronic state of the charge reservoirs. Each of the kinds of charge reservoir layers presently known has its own characteristic behavior in transferring charge to or from the CuO_x planes.

It is interesting to consider the crystal structures of some of the layered copper oxides in this context in somewhat more detail. In Table 1 are listed representative examples of the superconducting compounds with two CuO_2 layers. These include many of the best known superconductors. Next to each compound formula, the stacking sequence of one elementary structural unit is displayed. The stacking sequences which are responsible for the formation of the double CuO_5 pyramidal layers are the same for all the compounds: $-MO-CuO_2-M'-CuO_2-MO-$, where M and M′ are chosen (by nature) to satisfy geometric size and electronic charge balancing requirements. This sequence is broken in its middle for the entries in Table 1 to emphasize the sandwiching of the charge reservoir layers, shown in square brackets. The compounds have different numbers and kinds of layers in the charge reservoir sandwich, but when displayed as in Table 1, the close structural similarity among the different families of compounds described in the first part of this article is more transparent. Note that the last compound on the list, $La_2CaCu_2O_6$, is related to the others in terms of the active pyramidal copper layers, but has no charge reservoir layer. As in the family of compounds with a 2 : 1 ratio of A:Cu (Fig. 2), this compound could be doped by partial substitution of aliovalent cations on the $M^{3+}O$ layers. The compound $La_2CaCu_2O_6$ is, however, a puzzle to crystal chemists and physicists: it cannot be doped either by holes or electrons to induce metallic conductivity; no one knows why.

Table 1. Stacking sequences for superconductors based on two CuO_2 layers. Charge reservoir layers are shown in brackets.

Compound	Layer sequence						
$TlBa_2CaCu_2O_7$	$-Ca-CuO_2-BaO-[$		TlO		$]-$	$BaO-$	CuO_2-
$Tl_2Ba_2CaCu_2O_8$	$-Ca-CuO_2-BaO-[$	$TlO-$		$-TlO$	$]-$	$BaO-$	CuO_2-
$Ba_2YCu_3O_{6+\delta}$	$-Y-CuO_2-BaO-[$		$-CuO_\delta-$		$]-$	$BaO-$	CuO_2-
$Ba_2YCu_4O_8$	$-Y-CuO_2-BaO-[$	$CuO-$		$-CuO$	$]-$	$BaO-$	CuO_2-
$Pb_2Sr_2(Y,Ca)Cu_3O_{8+\delta}$	$-(Y,Ca)-CuO_2-SrO-[$	PbO	$-CuO_\delta-$	PbO	$]-$	$SrO-$	CuO_2-
$La_2CaCu_2O_6$	$-Ca-CuO_2-LaO-[$				$]-$	$LaO-$	CuO_2-

Although the structural relationships among the families shown in Table 1 are clarified by representation in this manner, the means by which the charge reservoir layers act electronically on the CuO_2 double planes is by no means straightforward. Each case is interesting in its own right. For the Tl-based materials, there is hybridization of Tl 6s and oxygen 2p orbitals, so the Tl certainly does not act as an ionic 3+ ion. Tl might in fact be expected to be covalently bonded to oxygen, with a formal charge between 1+ and 3+. This is probably what controls the charge on the CuO_2 planes. Indeed, if Tl acted straightforwardly as a 3+ ion, then one would expect no oxidation of copper in $Tl_2Ba_2CaCu_2O_8$. The doping occurs because Tl in the double Tl layer series acts as if its charge is $3 - \delta$, Cu is oxidized by the analogous amount $2 + \delta$ (*33*). The doping for the Bi analog $Bi_2Sr_2CaCu_2O_{8+x}$, surprisingly, may be different. Only two elements beyond Tl in the periodic table, Bi might display the same hybridization of its orbitals with O 2p orbitals. Bi, however, is expected to have a formal charge between +3 and +5, and therefore copper could possibly not be oxidized through the hybridization. Based on the solution of the crystal structure of the analogous compound $Bi_2Sr_3Fe_2O_{9+x}$, it has been proposed that excess oxygen is inserted into the Bi-O layers every fifth Bi atom. This excess oxygen supposedly oxidizes the Cu layers. To do that, the Bi-O layer must be unoxidizable, because the local charge picture would suggest that the oxygen should oxidize the cation in its local bonding environment. The Bi levels must be nowhere near the Fermi level, and hybridization with oxygen must be minimal. Thus, within this family, the charge reservoir layer acts differently depending on its chemistry. For the Tl-based compounds, charge is siphoned from the CuO_2 layer through the reduction of Tl, and for the Bi-based compounds through the transfer of charge from excess oxygen to the CuO_2 layers because there are no electronic states available to accommodate that charge within the BiO layers.

The compound $Ba_2YCu_3O_{7-x}$ is the most often studied of all high-temperature superconductors. Chemical studies have focused on the partial substitutions of many small metal atoms for Cu, and partial substitutions of a handful of large metal atoms for Ba and/or Y. Such substitutions are in general too disruptive of the basic crystal structure and magnetic/electrical state of the host to be of great help in understanding its intrinsic behavior. In the present context, a study of one such system, the $(Ba,La,Ca,Y)_3Cu_3O_x$ solid solution, has been interpreted in terms of a local charge type picture (*34*). The detailed study of the crystal structure and physical properties of oxygen-deficient $Ba_2YCu_3O_{7-x}$, however, has yielded the most unambiguous and complete information on the function of the charge reservoir layers in copper oxide superconductors, because it allows a comparison of structure and properties without severe disruption of the host. At first sight it seemed that the continuous removal of oxygen from the optimal $x = 0$ stoichiometry (the allowed range is $1 \geq x \geq 0$) afforded a straightforward way to study the variation of superconducting properties with copper valence. The changes in both structural and superconducting properties of $Ba_2YCu_3O_{7-x}$ with oxygen stoichiometry are, however, far from what would be expected from a simple continuous property variation with total charge content. The most dramatic indication that the situation was more complex came from the early observation of a distinct superconducting phase with a T_c of 60 K, and the now familiar two-plateau structure of T_c versus oxygen content for oxygen-deficient samples prepared at low temperatures [see, for instance (*35–40*)]. In addition, superconductivity disappears abruptly for homogeneous samples at a stoichiometry near $x = 0.45$, deceptively near the stoichiometry where the average copper valence is expected to be 2.0. The variation of the superconducting transition temperature with oxygen content for a typical series of oxygen-deficient $Ba_2YCu_3O_{7-x}$ samples (*35*) prepared by the low-temperature gettered annealing technique is presented in the top panel of Fig. 7.

For every oxygen removed from $Ba_2YCu_3O_7$, the electrons that were bonded to it (approximately two) must be transferred to the lowest unoccupied electronic energy level. The idea that the linearly increasing number of electrons that are dumped into the electronic bands with increasing oxygen deficiency should linearly decrease T_c (by continuously decreasing the hole population on the planes) assumes implicitly that the unoccupied energy levels are associated with the plane coppers only. This is not the case, which is an important manifestation of the presence of a charge reservoir layer and the relevance of local charge distribution.

One can learn about the local distribution of charge by considering the details of the crystal structures as a function of oxygen stoichiometry. These data are now available for the materials prepared at low temperatures (*41*). The metal-oxygen bond lengths in crystals are sensitive measures of the amount of charge in the chemical bonds between the atoms. There are several effective formulas from which the actual charge in a bond can be derived from the bond length, derived empirically from structural information on a large data base of well-characterized compounds. The sum of these charges (the "bond strengths") around a metal atom is its effective valence. We have calculated these bond valence sums for the copper atoms in $Ba_2YCu_3O_{7-x}$ prepared at low temperatures by means of the parameters derived by Brown (*42*), who has described the application to this system in considerable detail. The absolute values are accurate to 5%, but their precision within a well-defined series is considerably better. The bond valence sum, or valence, for the plane coppers in $Ba_2YCu_3O_{7-x}$ is shown in the lower panel of Fig. 7. The similarity of this curve to that of T_c versus x is clearly illustrated. Note that the bond valence sum changes in a nonlinear manner with oxygen content. The charge associated with the chain copper, however, does change linearly with oxygen deficiency.

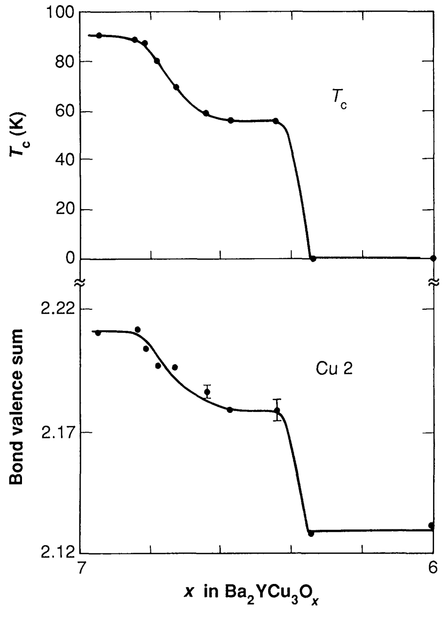


Fig. 7. (**Top**) Superconducting transition temperature (T_c) for $Ba_2YCu_3O_x$ prepared at low temperatures. (**Bottom**) Valence of the plane copper for the same samples determined from neutron diffraction crystal structure analysis.

The amount of charge associated with the plane copper shows the same two plateau behaviors as does T_c versus x. Thus the change from the 90 K to the 60 K superconductor is due to a gradual decrease of positive charge associated with the plane copper layer. The transition from the 60 K superconductor to the insulator involves an abrupt decrease in positive charge on the plane copper layer. Thus the structural data reveal a surprisingly complex series of transfers of local charge from the chain copper layers, from which the oxygens are removed, to the superconducting planar copper layers as a function of oxygen stoichiometry. At low oxygen deficiencies, the electrons formerly bonded to the oxygens are accommodated in electronic states associated entirely with the Cu-O chains. For oxygen deficiencies between approximately 0.2 and 0.3 electronic charge is gradually transferred into sites associated with the planes yielding a 60 K superconductor. Finally, near $x = 0.45$ further negative charge is abruptly transferred to the planes and superconductivity is lost. Thus the chain Cu-O layer acts as a complex charge buffer, controlling the amount of charge on the CuO planes and ultimately the material's T_c.

The compound $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ is a particularly interesting example of the manner in which local charge distribution controls the electronic properties of layered copper oxides. The crystal structure is shown in Fig. 6B. The host compound, with $x = 0$ and $\delta = 0$ is an antiferromagnetic insulator: the Pb is in a divalent state, the Cu between the PbO layers is monovalent, and the plane coppers are divalent. Under the normally oxidizing conditions employed to synthesize copper oxides the compound does not exist. That is because under such conditions the Pb is in a tetravalent state, and a lead-based perovskite is formed. The compound must be synthesized under mildly reducing conditions (N_2 gas at approximately 800°C). The compound, once formed, may be oxidized without decomposing at temperatures below 500°C. The oxygen is accommodated in the copper metal layers just as it is in $Ba_2YCu_3O_x$. The range of oxygen stoichiometry is large: up to 1.8 oxygens per formula unit can be obtained. Unlike the case of $Ba_2YCu_3O_x$, however, superconductivity is not induced, in spite of the fact that 3.6 additional positive charges ("holes") have been introduced to yield charge neutrality. This is because the excess oxygens oxidize only the Pb^{2+} and Cu^{1+} which are in the local cation array: The $PbO\text{-}CuO_\delta\text{-}PbO$ sandwich can accommodate a great deal of charge (5*e* per formula unit) by the oxidation of the Cu^{1+} to Cu^{2+} and Pb^{2+} to Pb^{4+}. The charge never gets transferred to the CuO_2 planes. The host material can, however, be made superconducting by partial replacement of the Y by Ca between the CuO_2 planes. In this case, the charge is accommodated by the oxidation of the CuO_2 layers, which are directly adjacent to the Y,Ca plane, to result in charge neutrality on a very local scale. Superconductivity occurs when the average formal valence of the copper in the plane is 2.25+. The superconducting compound then consists of oxidized copper and reduced copper and lead. This mixture of reduced and oxidized cations in the same crystallographic unit cell makes the choice of synthetic atmosphere difficult. Ambient atmospheres containing between 1 and 2% oxygen near 820°C are just reducing enough to keep the PbO-Cu-PbO sandwich reduced while oxidizing the planar coppers.

Conclusions

This brief review has described the crystal structures of the known copper-oxide superconductors from the particular viewpoint of their classification into structural families. It has also described, both in general and through the use of specific examples, the application of a local charge picture for understanding their electronic properties. The copper-oxide superconductors are of course primarily of interest to physicists and materials scientists for their revolutionary superconducting transition temperatures. In the time since their discovery, a sufficient number of new compounds have been synthesized to make them also of interest from a structural and crystal chemical point of view. Solid-state chemists can now think in terms of families of compounds, and apply the structural and chemical principles by which they are derived to look for new materials. Just as structural principals are essential, so is a framework by which to understand the electronic consequences of chemical composition and doping in materials with complex crystal structures. The local charge picture can provide such a framework, no doubt to be further revised as more compounds are discovered and old ones become better understood. As the field matures, and the probability of finding a new superconductor without knowing anything about solid-state chemistry becomes more unlikely, guided thinking and classification become more and more important for further progress in the search for higher T_c's.

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