

alkynes, and Clauss et al.⁵⁹ pointed out the conversion of an alkyne complex into a dialkylidyné complex either from theoretical analysis on cobalt or from experimental evidence on rhodium and iridium. If Ru, Co, Ir, and Mo behave differently than Ni, Pd, (W), it may be, as pointed out by Saillard et al.⁵⁸ from the plot of relative electron distribution as a function of electron count, that, at the right side of the transition series, surfaces should be negative relative to the bulk, and at the left side of the transition series, surfaces should be positive.

Our general conclusions will then be that possible surface intermediates in alkane reactions on metallic catalysts have only indirect proof in their support; however, they account for many experimental facts. We proposed an agostic precursor species which initiates the formation of σ -alkyl or carbene species to explain (a) the bond-shift, the cyclic, and the hydrogenolysis reactions; (b) less dehydrogenated species on the surface,^{35,45} in agreement with the kinetic model proposed by Frennet et al.,³¹ (c) dicarbyne mobility on the surface as proposed in ref 29. The $\alpha\gamma$ triadsorbed species proposed by Leclercq et al.⁶⁰ and Anderson et al.^{26,27,34}

can be rationalized with such an agostic precursor. Furthermore, the surface reconstructions of platinum single crystals by hydrogen correlated to change in the selectivity in isomerization and hydrogenolysis reactions reinforce the proposed agostic precursor.

More generally, our proposal for an agostic precursor species has the advantage of simplifying the interpretation of the different reaction mechanisms for isomerization and hydrogenolysis via a limited number of precursor species. It also allows us to account for the first steps of adsorption as well on platinum, palladium, and iridium catalysts as on bimetallic or alloy catalysts and agrees very well with the kinetic model proposed by Frennet,³⁰ where a reactive adsorption step occurs, followed by reactive surface dehydrogenation steps without any release of the sites occupied by adsorbed hydrogen.

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Structural Aspects of High-Temperature Cuprate Superconductors[†]

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Introduction

High-temperature superconductivity constitutes the most sensational discovery of recent times. Since these new superconductors are complex metal oxides, chemistry has had a big role to play in the investigations. For the first time, stoichiometry, structure, bonding, and such chemical factors have formed central themes in superconductivity, an area traditionally dominated by physicists. These oxide superconductors have given a big boost to solid-state chemistry.

C. N. R. Rao (born 1934) obtained his M.Sc. degree from Banaras, D.Sc. degree from Mysore, and Ph.D. and D.Sc. (honoris causa) degrees from Purdue. He is the founder-Chairman of the Solid State and Structural Chemistry Unit at the Indian Institute of Science, where he continues as a Professor and Director. He is a Fellow of the Royal Society, London, and a foreign honorary member of the American Academy of Sciences and Arts as well as of the Polish and U.S.S.R. science academies. He is a centennial foreign fellow of the American Chemical Society. His main research interests are solid-state chemistry of metal oxides, surface science, and chemical spectroscopy.

B. Raveau (born 1940) studied engineering as an undergraduate and obtained his doctorate degree in chemistry at Caen in 1966. He soon became professor at Caen, where he heads a flourishing school in solid-state chemistry. He now has an active team working on superconductivity and is collaborating with industry in developing devices. His main areas of interest are phosphate-bronze alloys, mixed-valent copper oxides, and applied solid-state chemistry.

The first group of high-temperature superconductors discovered¹ were oxides of the type $\text{La}_{2-x}(\text{Ca}, \text{Sr}, \text{Ba})_x\text{CuO}_4$ with T_c values in the 25–40-K range, soon followed by the so-called 123 oxides of the general formula $\text{LnBa}_2\text{Cu}_3\text{O}_7$ ($\text{Ln} = \text{Y}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{or Yb}$) with T_c values in the 90-K region. The chemistry of these two classes of oxide superconductors has been reviewed recently.²⁻⁷ The discovery of ma-

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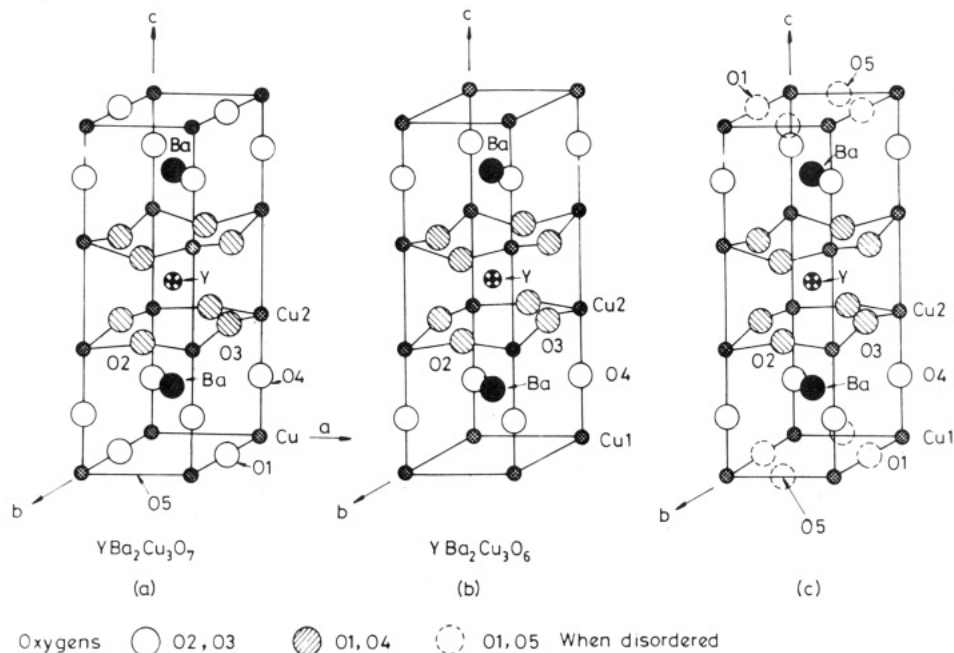


Figure 1. Structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: (a) $\delta = 0.0$, orthorhombic with oxygens ordered on O1 sites; (b) $\delta = 1.0$, tetragonal with fully depleted O1 sites; (c) disordered structure where both O1 and O5 sites are occupied.

terials with superconductivity above the liquid-nitrogen temperature has raised much hope and has prompted intensive search for new classes of oxides with still higher superconducting transition temperatures. Two new series of layered oxides belonging to the Bi-Ca-Sr-Cu-O and Tl-Ca-Ba-Cu-O systems and possessing the general formula $\text{A}_2\text{Ca}_{n+1-x}\text{B}_x\text{Cu}_n\text{O}_{2n+4}$ where A = Bi or Tl and B = Sr or Ba have been found to exhibit superconductivity between 60 and 125 K.⁶⁻¹⁸ A few members of the series ($n = 1-3$) of oxides have been characterized adequately, although there has been some difficulty in obtaining pure phases, especially in the bismuth cuprate system. The $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$ series of superconductors containing only a single Tl-O layer (compared to two Tl-O layers of the earlier series) is also known.^{15,18-20} Recently, superconducting lead

cuprates of the type $\text{PbASr}_2\text{Cu}_3\text{O}_{8+\delta}$ (A = Ln or Ln + Ca) have been discovered.²¹

It is noteworthy that all the high- T_c cuprates possess perovskite-related structures with covalent Cu-O bonds and exhibit some common features. In this Account, we present some of the significant structure-property relations in the various cuprate superconductors, distilled from the recent literature and substantially based on our own contributions to this area. In view of the immense literature on the subject, we shall cite only a few of the key references. We shall first present the essential features of the $\text{La}_{2-x}(\text{Ca},\text{Sr},\text{Ba})_x\text{CuO}_4$ and $\text{LnBa}_2\text{Cu}_3\text{O}_7$ systems²² and then discuss the bismuth and thallium cuprate superconductors. We shall then highlight the structural relationships as well as the commonalities among the different superconducting cuprates and examine the states of copper and oxygen ions in the cuprates. We shall point out how oxygen holes play a role in the superconductivity. The involvement of oxygen constitutes an important new idea that needs to be explored further. That the oxygen holds the key to the superconductivity of oxides is also substantiated by the discovery of relatively high T_c (~ 30 K) superconductivity in oxides such as $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ not containing copper.²³

Some Important Features of $\text{La}_{2-x}(\text{Ca},\text{Sr},\text{Ba})_x\text{CuO}_4$ and $\text{LnBa}_2\text{Cu}_3\text{O}_7$ ²²

$\text{La}_{2-x}\text{Ba}_x(\text{Sr}_x)\text{CuO}_4$ compounds have the quasi-two-dimensional K_2NiF_4 structure with tetragonally elongated Cu-oxygen octahedra; the Cu ions can interact

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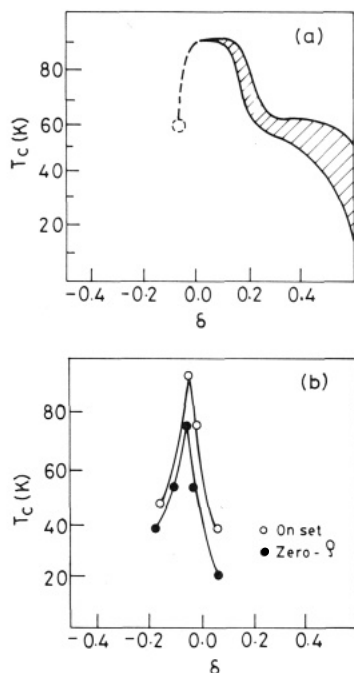


Figure 2. Variation of T_c with δ in (a) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and (b) $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Shaded region includes data from different sources.

only in the ab plane. These oxides have a tetragonal structure at room temperature when $x > 0.05$ and become orthorhombic around 180 K, well above the superconducting transition temperature (25–40 K). T_c in these oxides shows a maximum around a specific value of x (~ 0.15 and 0.2 respectively in the case of Ba and Sr), around which compositions certain structural parameters also seem to show anomalous features. Parent La_2CuO_4 ($x = 0$) is itself orthorhombic and becomes superconducting ($T_c \sim 30$ – 40 K) when it has an oxygen excess or a lanthanum deficiency. The La ion in $\text{La}_{2-x}\text{Ba}_x(\text{Sr}_x)\text{CuO}_4$ can be replaced by rare earth ions such as Pr, Nd, Eu, and Gd up to a point ($< 10\%$) without losing superconductivity, although T_c is generally lowered. Substitution of Cu partly by Ni and Zn also lowers the T_c .

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and related 123 oxides are orthorhombic (Figure 1), by virtue of the preferential population of the O1 sites (along the b axis) giving rise to Cu–O chains. A disordered orthorhombic structure can result if both the O1 and O5 sites are occupied (but unequally). A tetragonal structure results if the O1 oxygens are depleted extensively or the O1 and O5 sites are equally occupied. The tetragonal–orthorhombic transition is responsible for the formation of twins; across the twin boundary, the Cu–O chain direction is rotated by 90° . The orthorhombic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ continues up to $\delta \approx 0.6$ when the structure becomes tetragonal; $\text{YBa}_2\text{Cu}_3\text{O}_6$ is tetragonal and nonsuperconducting. The T_c of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ shows an interesting variation with δ . The T_c is ~ 90 K up to $\delta \approx 0.20$; there is a plateau in T_c (55 ± 5 K) in the δ range of 0.20 – 0.40 (Figure 2). The material becomes nonsuperconducting at $\delta \approx 0.6$. The orthorhombic structure can be extended to higher values of δ by low-temperature gettering, but the T_c values of such samples are rather low (≤ 40 K). Since the structure in the plateau region is orthorhombic, the possible occurrence of oxygen vacancy ordering has to be examined. While some evidence for vacancy ordering has

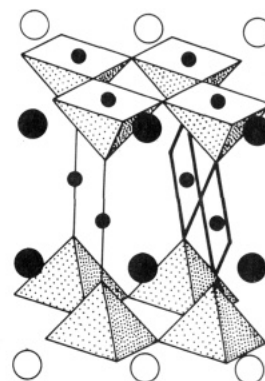


Figure 3. Intergrowths of superconducting "O₇" domains (CuO_4 square-planar groups) and insulating "O₆" domains (Cu in 2-fold coordination).

been found in electron-diffraction patterns, it seems to depend on the method of preparation of the samples. Such compositions can be mixtures of orthorhombic O₇ and tetragonal O₆ structures. More interestingly, intergrowths of O₇ and O₆ structures can occur in compositions with $\delta \geq 0.50$. Occurrence of superconductivity ($T_c \leq 45$ K) in these compositions (especially $\delta \approx 0.5$) is better explained by intergrowths of domains that are alternately superconducting and insulating according to the formulation $\text{YBa}_2(\text{Cu}_2^{2+}\text{Cu}^{3+}\text{O}_7)_{1-x}(\text{Cu}_2^{2+}\text{Cu}^{1+}\text{O}_6)_x$.²⁴ In Figure 3 we illustrate the nature of the intergrowth structure of O₇ and O₆ units suggested by electron microscopic observations.

Unlike in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ becomes tetragonal for relatively small deviations from stoichiometry ($|\delta| < 0.1$). Oxygen-excess $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples are more readily obtained than in the yttrium system, but these are almost always tetragonal and nonsuperconducting. High T_c (~ 77 K) in $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is found only when $\delta \approx 0.0$ (Figure 2), at which composition the structure is orthorhombic.^{6,25} The sensitivity of T_c to δ in $\text{LnBa}_2\text{Cu}_3\text{O}_7$ depends on the Ln (rare earth) ion. A plateau at lower T_c (~ 50 K) is seen for $\delta > 0.2$ when Ln = Gd or Dy as well, but the orthorhombic structure in this δ region is different from that in the 90 K T_c region ($b = c/3$). All $\text{LnBa}_2\text{Cu}_3\text{O}_7$ compounds become tetragonal above a certain temperature (e.g.: La, 590 K; Y, 970 K). The larger Ln ions can readily interchange sites with Ba, unlike the smaller ions. This is also true of the more general $\text{Ln}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+y}$ family of which the 123 oxides are the $x = 1$ members. In the 336 family, the structural dependence (orthorhombic/tetragonal) on x depends on the Ln ion; oxygen-excess compositions of the 336 family generally possess tetragonal structures.^{6,26}

A variety of studies have been carried out to investigate the effect of substituting Y, Ba, or Cu by other metal ions. The Cu ion in $\text{YBa}_2\text{Cu}_3\text{O}_7$ can be replaced by cations such as Zn and Fe, and these substitutions generally tend to give rise to tetragonal structures accompanied by changes in oxygen stoichiometry and lower T_c values.²⁷ While most high- T_c (~ 90 K) 123

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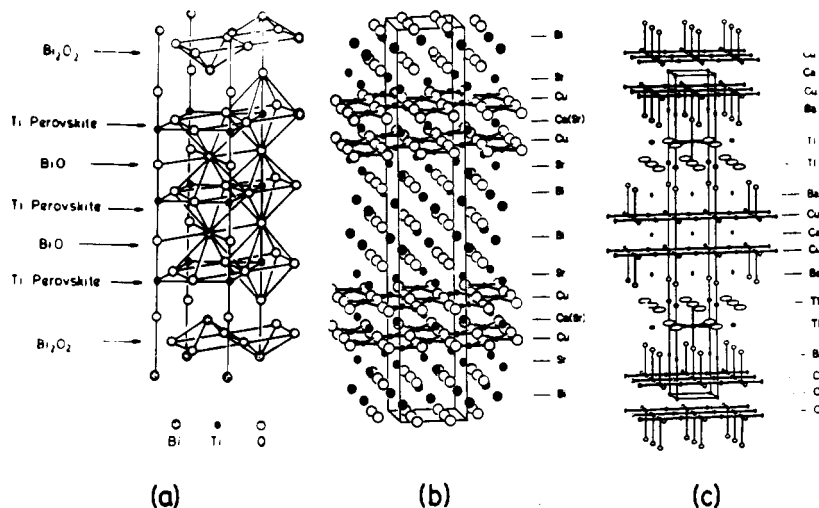


Figure 4. Comparison of the structures of (a) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (Aurivillius phase), (b) $\text{Bi}_2(\text{Ca,Sr})_3\text{Cu}_2\text{O}_8$ (after Subramanian et al.¹¹), and (c) $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$ (after Subramanian et al.³⁴).

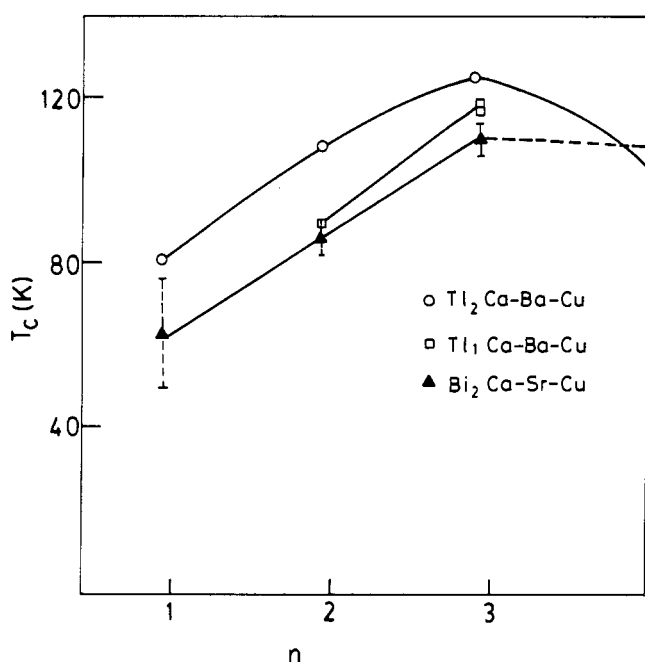


Figure 5. Variation of T_c in Bi and Tl cuprates with the number of Cu-O layers, n .

oxides are orthorhombic, certain tetragonal 123 compositions with high T_c values have been prepared.^{28,29} Orthorhombicity is not a necessary criterion for high T_c . The tetragonal superconducting samples, however, show orthorhombic microdomains in electron micrographs. $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is orthorhombic, but not superconducting.³⁰

When Ba in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is progressively replaced by Sr, the T_c is lowered. Substitution of Y by Pr has a similar effect until superconductivity is lost at $\sim 60\%$ Pr. In $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$, the structure becomes tetragonal with increase in x and the T_c of the orthorhombic phase decreases with increase in x . The lability of oxygen is reduced by partial substitution of Ba by

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La, a factor that may be useful in materials processing.³¹ In oxides such as $\text{GdBa}_2\text{Cu}_3\text{O}_7$, superconductivity coexists with magnetism.³²

Bi-Ca-Sr-Cu-O and Tl-Ca-Ba-Cu-O Systems^{6-20,33-42}

After the initial report of superconductivity (maximum $T_c \approx 22$ K) in $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$ by Michel et al.,³³ Maeda et al.⁸ reported high T_c with onset in the 100 K region in a Bi-Ca-Sr-Cu-O composition. Since then, several compositions of the Bi-Ca-Sr-Cu-O system belonging to the $\text{Bi}_2(\text{Ca,Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4}$ series have been investigated widely. The $n = 2$ member of this series, $\text{Bi}_2(\text{Ca,Sr})_3\text{Cu}_2\text{O}_{8+\delta}$, with zero-resistance T_c of ~ 90 K, has been characterized by several workers both in polycrystalline and single-crystal forms. The exact composition of the phase, however, seems to vary from one laboratory to another. The $n = 2$ member seems to be the most stable phase in this series. The bismuth cuprates are orthorhombic and have structures somewhat similar to those of the Aurivillius family of oxides,

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$(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$. In Figure 4, we compare the structures of $\text{Bi}_2\text{Tl}_3\text{O}_{12}$ and $\text{Bi}_2(\text{Ca,Sr})_3\text{Cu}_2\text{O}_8$, both of which have similar c parameters in the region of 30 Å. The main difference is that the cuprate does not have Bi_2O_2 layers, but instead has BiO layers separated by ~ 3.25 Å; cleavage between the two layers yields charge-neutral sections.¹¹ This is probably why the bismuth cuprates have mica-like morphology. The Cu coordination, although pyramidal, tends to be essentially square-planar in $\text{Bi}_2(\text{Ca,Sr})_3\text{Cu}_2\text{O}_8$ and O_6 .³⁵ Electron micrographs of Bi-Ca-Sr-Cu-O oxides clearly show evidence for modulation in the structure; superlattice structures are seen in the diffraction patterns. The micrographs also show the presence of extensive dislocations and intergrowths of different layered sequences.

While most workers have characterized the $n = 2$ member of the Bi-Ca-Sr-Cu-O system, there has been considerable difficulty in obtaining pure monophasic materials especially of the $n = 3$ member.³⁶ $\text{Bi}_2\text{CaSrCuO}_{6+\delta}$ ($n = 1$) has a T_c of 60 ± 20 K, the actual value depending on the Ca/Sr ratio. We find that starting Ca-rich compositions tend to yield more monophasic products. Initial reports of two T_c values around 80 and 110 K in some of the compositions as well as the occurrence of very low T_c in some others are clearly due to the presence of different phases. While very low T_c values could arise from $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$ and such phases, the ~ 110 -K T_c is almost certainly due to the presence of a small proportion of the $n = 3$ member.³⁶ $\text{Bi}_2(\text{Ca,Sr})_4\text{Cu}_3\text{O}_{10+\delta}$ (up to $\sim 20\%$) in mixture with the $n = 2$ member shows a T_c of ~ 105 K.³⁷ Pure $n = 3$ member ($T_c \sim 105$ – 110 K) has been characterized recently; substitution of Bi by Pb (up to 25%) favors the formation of this phase.¹²

On the basis of the characterization of a variety of compositions of the Bi-Ca-Sr-Cu-O system, it appears that the T_c values of the $n = 1, 2,$ and 3 members are around $60 \pm 20, 85 \pm 5,$ and 107 ± 3 K, respectively,¹² the orthorhombic c parameters being $\sim 25, 31,$ and 37 Å, respectively. The T_c clearly increases with the number of Cu-O layers up to $n = 3$ (Figure 5). The $n = 4$ member, synthesized recently, has a T_c only slightly higher than that of the $n = 3$ member.¹² It appears that T_c does not increase with the number of CuO sheets beyond three. Attempts have been made to synthesize recurrent intergrowth structures,³⁸ involving a periodic arrangement of different layered phases at the unit-cell level. Unfortunately, it has not been possible to prepare such ordered intergrowth structures involving members of the $\text{Bi}_2(\text{Ca,Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4}$ series, unlike in the case of the Aurivillius family of bismuth oxides.³⁸

Superconductivity in the Tl-Ca-Ba-Cu-O system was first reported by Sheng and Hermann.¹³ These tetragonal oxides have the general formula $\text{Tl}_2\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+4}$. In this series, $\text{TlBa}_2\text{CuO}_6, \text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8,$ and $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ corresponding to $n = 1, 2,$ and 3 with c parameters of $\sim 23, 29,$ and 36 Å respectively are known to show T_c values of around 80, 110, and 125 K. Structures of the Tl-Ca-Ba-Cu-O superconductors are similar to those of the Bi-Ca-Sr-Cu-O system. In Figure 4, we compare the structure of $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$ with that of $\text{Bi}_2(\text{Ca,Sr})_3\text{Cu}_2\text{O}_8$. These thallium cuprates have essentially corner-sharing

square-planar CuO_4 groups oriented to the (001) planes just as in the bismuth cuprates, but the copper-oxygen polyhedra are more distorted in the latter. There are no oxygen atoms between the Cu-O sheets. The Cu-O distance in $\text{Tl}_2\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+4}$ decreases with increase in n , accompanied by a small decrease in the a parameter; the intersheet Tl-O bonds are ~ 2.0 Å in length, and the separation between two Tl layers is 2.2 Å.^{34,39} Crystals of the Tl cuprates are therefore difficult to cleave and are rod-shaped. Increasing the T_c in the Tl-Ca-Ba-Cu-O system to much higher temperatures by increasing n seems difficult since the $n = 4$ member has a T_c of 104 K.⁴⁰ Electron-diffraction patterns of the $n = 5$ member have been obtained, but the pure phase has not been isolated. Electron micrographs show defects and intergrowths of different sequences in the Tl cuprates as well.

The $n = 2$ and 3 members of the $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+4}$ series containing only one Tl-O layer have been isolated and characterized.^{14,19-21} These oxides have T_c values lower than those of corresponding members of the $\text{Tl}_2\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+4}$ series (Figure 5), suggesting a role for the Tl layers. Recently, members of the $\text{Tl}_{1-x}\text{Pb}_x(\text{Ca,Sr})_{n+1}\text{Cu}_n\text{O}_{2n+3}$ series of high- T_c superconductors have been characterized; substitution of Ca partly by Y in Tl and Bi cuprates lowers the T_c markedly.⁴¹ $\text{TlCa}_{0.5}\text{Ln}_{0.5}\text{Sr}_2\text{Cu}_2\text{O}_y$ ($\text{Ln} = \text{Y}$ or rare earth), however, represents a series of 1122-type superconductors ($T_c \sim 90$ K).

Structural Relationships in the Cuprates

A feature common to all the high- T_c cuprate superconductors is the high covalency of the Cu-O bonds and the two-dimensional character of the copper-oxygen framework closely related to that of the perovskites. Thus, $\text{La}_{2-x}(\text{Ca,Sr,Ba})_x\text{CuO}_4$ as well as the Ba-Ca-Sr-Cu-O and Tl-Ca-Ba-Cu-O oxides can be considered to belong to the same structural family involving the intergrowth of multiple oxygen-deficient perovskite layers, ACuO_{3-x} , with rock-salt-type layers, AO , leading to the general formula $[\text{ACuO}_{3-x}]_n[\text{AO}]_{n'}$. $\text{La}_{2-x}\text{M}_x\text{CuO}_4$,^{1,5} $\text{Bi}_2\text{Sr}_2\text{CuO}_6$,³³ and $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ ¹³ represent the $n = 1$ members formed of single perovskite layers according to the formulas $[\text{La}_{1-x}\text{M}_x\text{CuO}_{3-\delta}]$ -, $[\text{La}_{1-y}\text{M}_y\text{O}]$, $[\text{SrCuO}_3][(\text{BiO})_2(\text{SrO})]$, and $[\text{BaCuO}_3]$ -, $[(\text{TlO})_2(\text{BaO})]$. They differ from one another in the thickness of the rock-salt-type layer. One indeed observes single $[\text{La}_{1-y}\text{M}_y\text{O}]_\infty$ layers in La_2CuO_4 -related oxides (Figure 6a) and triple rock-salt layers ($n' = 3$) in the other two oxides (Figure 6b) formed by a monolayer of $[\text{SrO}]$ or $[\text{BaO}]$ and bilayers of $[(\text{BiO})_2]$ or $[(\text{TlO})_2]$. The $n = 2$ members are represented by the three oxides $\text{TlCaBa}_2\text{Cu}_2\text{O}_7$,¹⁸⁻²⁰ $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$,^{9,11,36,40} and $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$.^{14,34,41} Here, the double oxygen-deficient perovskite layers ($n = 2$) are formed by two layers of corner-sharing CuO_5 pyramids interleaved with a plane of Ca ions leading to the formulas $[\text{CaBa}(\text{CuO}_{2.5}\square_{0.5})_2][(\text{BaO})(\text{TlO})]$, $[\text{CaSr}(\text{CuO}_{2.5}\square_{0.5})_2]$ -, $[(\text{SrO})(\text{BiO})_2]$, and $[\text{CaBa}(\text{CuO}_{2.5}\square_{0.5})_2][(\text{BaO})(\text{TlO})_2]$, where \square represents an oxygen vacancy. Thus, $\text{TlCaBa}_2\text{Cu}_2\text{O}_7$ (Figure 6c) exhibits a double rock-salt layer ($n' = 2$) formed of monolayers of (BaO) and (TlO) whereas triple rock-salt layers ($n' = 3$) formed of double $[(\text{BiO})_2]$ or $[(\text{TlO})_2]$ and a monolayer of $[\text{SrO}]$ or $[\text{BaO}]$ are present in $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ and $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$ (Figure 6d). Triple oxygen-deficient perovskite layers

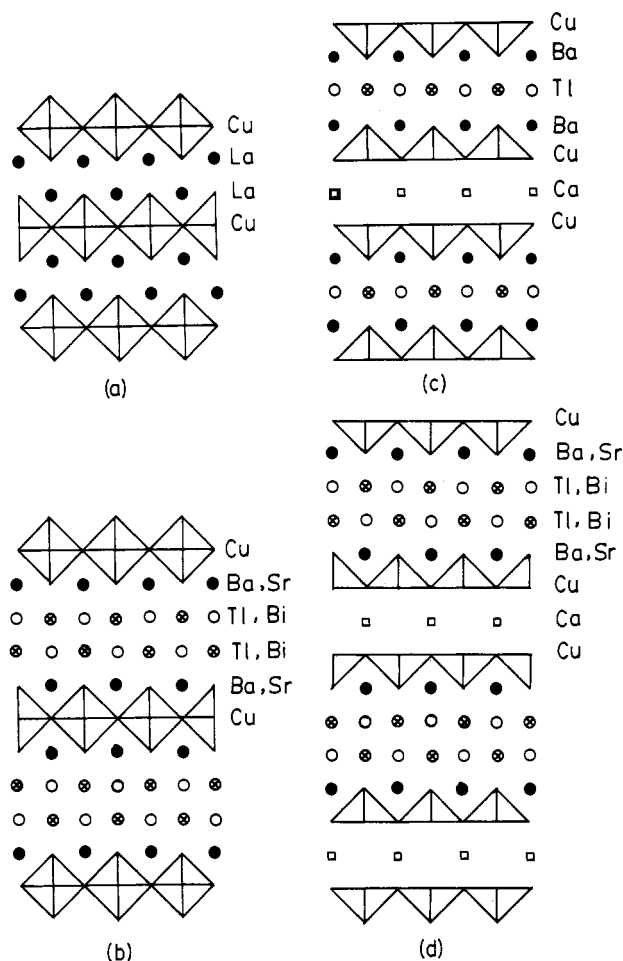


Figure 6. Schematic representations of the structures of (a) La_2CuO_4 -type oxides, (b) $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ and $\text{Tl}_2\text{Ba}_2\text{CuO}_6$, (c) $\text{TlCaBa}_2\text{Cu}_3\text{O}_7$, and (d) $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ and $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$. Oxygens are shown by open circles and Bi and Tl by circles with a cross.

($n = 3$) are obtained in $\text{TlCa}_2\text{Ba}_2\text{Cu}_3\text{O}_9$,^{14,20} $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$,^{17,39,42} and $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$.^{12,36,37} In these structures, the triple perovskite layer is formed by one layer of corner-sharing CuO_4 square-planar groups sandwiched by two layers of corner-sharing CuO_5 pyramids; two planes of Ca ions are interleaved between these layers. There are two rock-salt layers ($n' = 2$) in $\text{TlCa}_2\text{Ba}_2\text{Cu}_3\text{O}_9$ and three ($n' = 3$) in the other two oxides are illustrated in Figures 7a and 7b, respectively. Thus, the general formula of these three oxides can be written as $[\text{BaCa}_2(\text{CuO}_{2.5}\square_{0.5})_2(\text{CuO}_2\square)][(\text{AO})_{10r2}(\text{BO})]$, where $\text{B} = \text{Sr}$ or Ba and $\text{A} = \text{Bi}$ or Tl .

It is worth noting that the rock-salt layers, (TlO) and (BiO), are distorted compared to $\text{La}_{1-y}\text{M}_y\text{O}$ layers in La_2CuO_4 -type oxides. The (TlO) layers are much less distorted than the (BiO) layers; the distance between two layers is indeed much larger in the latter. The $[\text{CuO}_2]_\infty$ layers of corner-sharing CuO_4 square-planar groups forming the basal planes of the octahedra or square pyramids are much less puckered in the La_2CuO_4 -type oxides and in the thallium cuprates compared to the bismuth cuprates. This behavior of bismuth cuprates may be associated with the lone pair ($6s^2$) of bismuth, which may also be responsible for the modulation of the structure.

$\text{YBa}_2\text{Cu}_3\text{O}_7$ and related 123 oxides can be considered to constitute the $n' = 0$ members of the general structural class of oxygen-deficient perovskites described

above. The ordering of oxygen and anionic vacancies in the perovskite framework (Figure 7c) leads to a layer structure that bears considerable similarity to the other cuprates. We can recognize similar layers of corner-sharing CuO_5 pyramids interleaved with planes of yttrium ions. The main difference in the 123 oxides is that two pyramidal layers are connected through rows of corner-sharing CuO_4 square-planar groups resulting in the formulation $[\text{YBa}(\text{CuO}_{2.5}\square_{0.5})_2][\text{BaCuO}_2\square]$. $\text{YBa}_2\text{Cu}_3\text{O}_8$ (124) with two CuO chains ($T_c \sim 80$ K) is also known.⁴³

States of Copper and Oxygen

Superconducting $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ and $\text{LnBa}_2\text{Cu}_3\text{O}_7$ would nominally be expected to contain a fair proportion of Cu^{3+} ions. Such a nominal Cu(II)-Cu(III) mixed valence has been considered to play an important role in the superconductivity of these oxides. Superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ cannot be explained by taking into account the charge balance based on elementary chemical considerations alone. Thus, $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, which should formally contain only Cu(II) , should not be superconducting, but it shows a T_c of ~ 45 K. A possibility is that there is intergrowth of O_7 and O_6 domains as suggested earlier, requiring the presence of Cu(III) , Cu(II) , and Cu(I) states. What is interesting is that the T_c values of the La_2CuO_4 -type oxides as well as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ show a proportional increase from 30 to 90 K with the nominal $\text{Cu}^{3+}/\text{Cu}(\text{total})$ ratio (Figure 8). However, this would not be the case in the Bi and Tl cuprates. We do not as yet fully understand the role of nonstoichiometry as well as of the TlO and BiO layers in the superconductivity of these cuprates.

Considerable effort has been made to understand the nature of copper and oxygen ions in the different cuprates since all the essential phenomena (magnetic properties and superconductivity) are confined to the CuO_2 sheets. It is well understood that localized Cu^{3+} ions cannot exist in the structures of these cuprates.^{5,44} The excess positive charge (holes) is likely to be delocalized over the Cu-O framework as indicated by the metallic behavior of the cuprates. An important question that arises is whether the holes appear mainly on copper leading to the Cu(III) state (d^8 electron configuration) or whether they appear elsewhere. The answer from electron and X-ray spectroscopic studies is that all the excess holes end up as holes in the oxygen band or O^{1-} with $2p^5$ electronic configuration.

On the basis of X-ray absorption (Cu K or L edge) spectroscopy, many workers initially came to the conclusion that Cu^{3+} was present in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$. Later measurements have, however, shown this not to be correct. The presence of a Cu^9 -ligand hole state has been established by X-ray absorption spectroscopic studies; a $1s \rightarrow 2p$ transition in the oxygen-edge spectrum confirms the presence of holes in the oxygen band, and this has also been verified by electron energy loss spectroscopy.⁴⁵⁻⁴⁷

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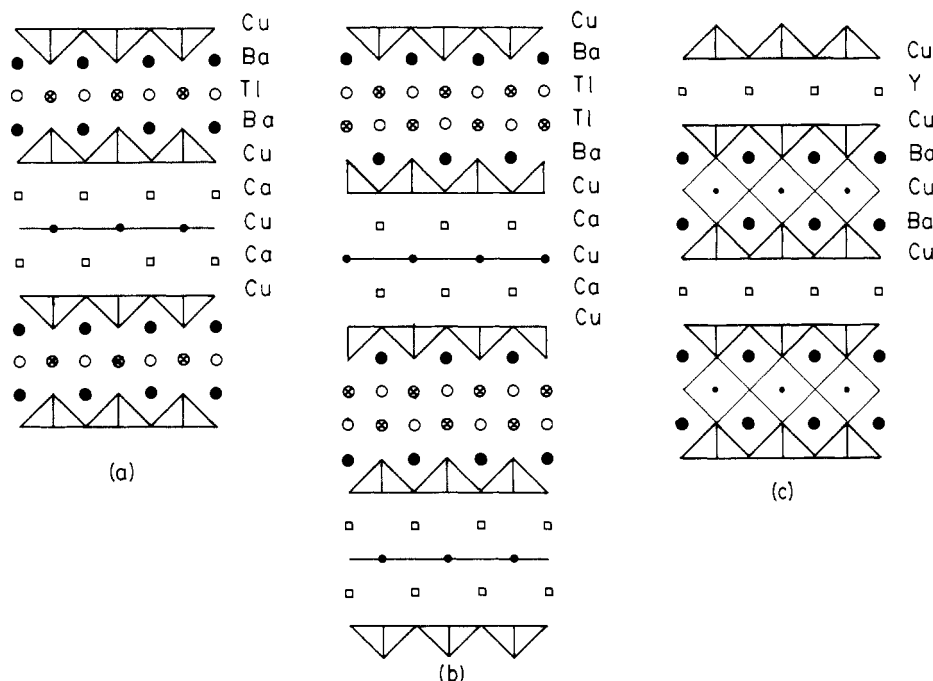


Figure 7. Schematic representations of (a) $\text{TlCa}_2\text{Ba}_2\text{Cu}_3\text{O}_9$, (b) $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$, and (c) $\text{YBa}_2\text{Cu}_3\text{O}_7$.

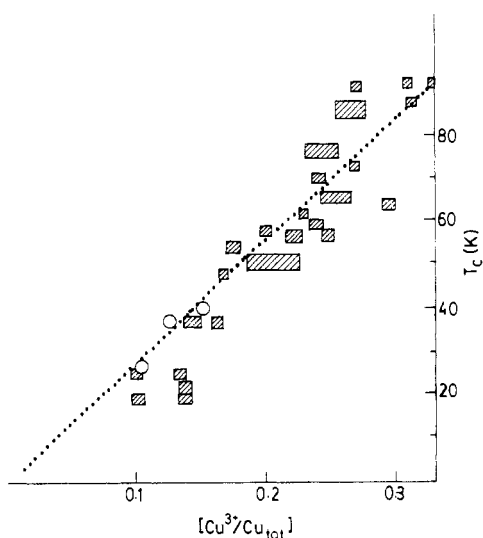


Figure 8. Variation of T_c with the nominal $\text{Cu}^{3+}/\text{Cu}(\text{total})$ ratio in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (hatched rectangles) and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (circles). The hatched rectangles include data of a number of workers.

We have investigated the nature of holes in the superconducting cuprates for some time by employing X-ray photoelectron (XP) and Auger electron spectroscopies.^{48,49} $\text{Cu}(2p)$ X-ray photoelectron and $\text{Cu } L_3VV$ Auger spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ as well as the Bi and Tl cuprates show the presence of only the Cu^{1+} and Cu^{2+} species in the ground state of these oxides, with no detectable amount of Cu^{3+} .

The $\text{O}(1s)$ core-level spectra of the cuprates show the presence of features with binding energies of around 529, 531, and 533 eV, respectively.⁴⁸ The normally expected oxide species, O^{2-} , with the filled $2p^6$ configu-

ration is associated with the 529-eV feature. The O^{1-} species (corresponding to the presence of a hole in the $2p$ band) is expected to have a higher binding energy than O^{2-} , but the position of this $\text{O}(1s)$ feature is likely to be in the 529–531 region. Unfortunately, CO_3^{2-} and OH^- , which are almost always present in such oxides, give an intense peak around 531 eV. We, however, find an oxygen species with a binding energy of 533 eV which could be considered to be due to the dimerization of O^{1-} holes giving peroxide-like species. The proportion of the dimerized holes seems to increase substantially with decreasing temperature, and the phenomenon is reversible.^{48,49} Although there is some uncertainty regarding the assignment of the 533-eV feature, it should be noted that a few other workers have recently assigned this to peroxide-like species.^{50,51} The dimerized hole species could play an important role in the mechanism of superconductivity of these oxides. The presence of Cu^{1+} in the superconducting state of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ dictates that a considerable proportion of the oxygens be present in the hole state. Furthermore, the $d^{10}(\text{Cu}^{1+})$ state favors such oxygen holes.⁵² It is interesting that Takura et al.⁵³ have recently correlated T_c of the cuprates with the $[\text{Cu}-\text{O}]$ charge in the sheets. The charge, p , of $(\text{Cu}^{z+}-\text{O}^{m-})^p$ is determined by z and m ; since $z \neq 3$, we can only have (a) $(\text{Cu}^{2+}\text{O}^{1-})^{1+}$, (b) $(\text{Cu}^{2+}\text{O}^{2-})^0$, and (c) $(\text{Cu}^{1+}\text{O}^{1-})^0$ species. It seems possible that the relative proportions of b and c will determine whether a particular oxide is superconducting or insulating for a given charge, p . It is noteworthy that the new superconducting lead cuprates²¹ are required to

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have a reasonable proportion of Cu^{1+} by virtue of their stoichiometry.

Concluding Remarks

We have attempted to point out the common structural features of the different families of cuprate superconductors. Besides being structurally related, we have shown that the cuprates are likely to have a common mechanism of superconductivity involving holes on oxygen. These holes seem to have mainly p_σ character.^{49,54} Such holes may also be present in many other transition-metal oxides, especially those where the d electrons are itinerant.^{49,52}

There are many chemical aspects of the oxide superconductors that are yet to be fully understood. Many new classes of oxides as well as other materials are yet to be explored. There are indications that many simple oxide systems may show superconductivity;

other layered systems with Lu, Ga, In, etc., are yet to be explored. One possible strategy to follow would be to synthesize oxides or possibly other chalcogenides where anionic holes are favored. Chemically this means that we need to have systems with small anion to metal charge-transfer energy. Instead of being in a high oxide state, the metal would rather accept electrons from the anion (oxide) and create an anion (oxygen) hole. Besides oxides containing Bi and Pb, it would be worth investigating oxides containing Ni, V, Nb, Ti, Zr, Pd, and so on. There is also need to investigate three-dimensional oxide systems for superconductivity since $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ has a T_c of ~ 30 K.²³ There is every hope that chemists will one day find a material with T_c close to room temperature. Their synthetic skills⁵⁵ will be of great value in this gold rush.

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