JOURNAL OF SOLID STATE CHEMISTRY **80**, 142–146 (1989)

# On the Involvement of Apical O in CuO-Based Superconductors

H. OESTERREICHER

*Department of Chemistry, University of California at San Diego,*
*La Jolla, California 92093*

Received January 30, 1989

A model based on spectroscopic evidence for holes residing on O in CuO-based superconductors is discussed. Accordingly, superconductivity stems from two separate species, namely O in the $CuO_2$ planes ($^pO$) and O is apical positions ($^aO$, located in BaO planes in $YBa_2Cu_3O_x$). In $YBa_2Cu_3O_x$, this leads to two separate phases with $T_c \sim 60$ and $T_c \sim 90$ K, respectively, as these two species become successively oxidized. Predictions are made concerning the behavior of compound families such as $Bi_2Sr_2Ca_{n-1}Cu_nO_x$. For a given $n$, two separate superconducting phases should potentially generally obtain as a function of increasing hole concentration with $T_c$ ratios reflecting the ratios of $^pO/^aO$. © 1989 Academic Press, Inc.

## Introduction

We discuss in the following a model according to which two contributions to superconductivity can exist in CuO-based superconductors (see (*1*) for review and $T_c$ data), namely one from O in $CuO_2$ planes ($^pO$) and one from apical O ($^aO$). The latter are O atoms coordinated in the plane with Ba in $YBa_2Cu_3O_x$. These two species are generally found in CuO-based ceramic superconductors and we shall attempt to show that their relative amounts and oxidation states dictate the magnitude of the superconducting transition temperature. Both types of O are a result of perovskite stacking. As outlined earlier (e.g., Ref. (*2*)), the simple cubic perovskite stacks a $M^{2+}O$ (B site) layer on top of a $M^{4+}O_2$ (A site) layer which is turned by 90°. This general principle is maintained in complex superconducting perovskites. As examples in compound series such as $YBA_2Cu_nO_x$, $Bi_2Sr_2Ca_{n-1}Cu_nO_x$, or their Tl analogs, $(CuO_2)n$ planes are followed by alkaline earth oxide planes (e.g., BaO as B site analogs). The $CuO_2$ planes are the source of the $^pO$ and the B sites produce $^aO$. More specifically, the $YBa_2Cu_3O_x$ stacking can be written as ($^pCu$ $^pO_2$) (Y) ($^pCu$ $^pO_2$) (Ba $^aO$) ($^cCuO$) (Ba$^aO$) where $^cCu$ or chain Cu is stacked symmetrically between BaO planes. Increasing $x$ results in a rise in $T_c$ with two plateaus of ~60 and ~90 K, respectively (e.g., Refs. (*3, 4*)). Formally speaking, $^cCu$ is 1+ with $x = 6$ and rises to 3+ with $x = 7$. In reality, this charge is partly delocalized beyond $x = 6.5$ and holes can be found on O (*5*). Superconductivity is now considered to require $CuO_2$ planes

0022-4596/89 $3.00

Copyright © 1989 by Academic Press, Inc.
All rights of reproduction in any form reserved.

only rather than chains (e.g., as many chainless compounds are superconductors) and the mechanism for $T_c$ plateaus should be connected with regions near these planes. We shall in the following present pertinent data and subsequently discuss them in the frame of our model.

## Results

We take as our point of departure the findings that in $YBa_2Cu_3O_x$ two superconducting modifications exist with $T_c \sim 60$ and $T_c \sim 90$ K, respectively, as schematically shown in Fig. 1 together with proposed valencies (spinoidal decompositions have been implicated (*6*) in producing these plateaus, but the preparation temperatures and details of the magnetic signals in question rule this out at least for the materials in Refs. (*3*, *4*)). A series of papers on partly substituted materials (*4*, *7*, *8*) have shown that electron filling is responsible for plateaus in $T_c$ rather than the O filling $x$. As an example, $T_c \sim 90$ K can be obtained with relatively low $x$ in compounds such as $Y_{1-y}M_yBa_2Cu_3O_x$ with $M$ = Ca or Na. This rules out the implications of superstructure in ${}^cCuO$ or any of its local configurations. In order to explain the existence of plateaus in $T_c$, we must assume that systems (such as ${}^cCu$) other than the one supporting superconductivity gradually change in charge with $x$. We assume, therefore, that ${}^cCuO$ stays insulating and functions as a charge buffer while the mechanism providing $T_c$ plateaus must be in the plane or its vicinity.

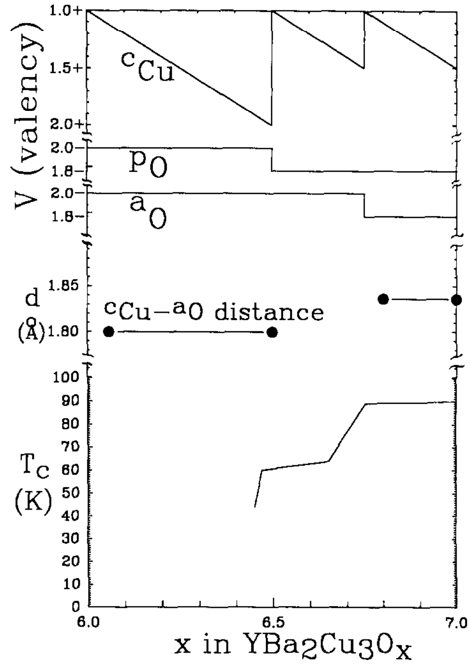

FIG. 1. Schematic representation of superconducting transition temperatures ($T_c$), distance ${}^cCu$ ${}^aO$ ($d$) and valencies, ($v$), as a function of $x$ in $YBa_2Cu_3O_x$. Data are from Refs. (*3*, *4*). Valencies are calibrated to assumptions given in the text. Actual hole to O ratios may be closer to 1 : 12 rather than 1 : 4 assumed here. No data are available for $d{}^cCu{}^aO$ between $x = 6.5$ and $x = 6.75$ and the specific sample with $x = 0.5$ was not yet superconducting.

The mechanism behind charge delocalization is outlined in the following schematic representation. Accordingly, we write formally $(Y\ {}^pCu_2^{2+}\ {}^pO_4)^{-1}(Ba_2\ {}^aO_2)({}^cCu^{1+}O_0)^{1+}$ for $x = 6$ and $(Y\ {}^pCu_2^{2+}\ {}^pO_4)^{-1}(Ba_2\ {}^aO_2)({}^cCu^{3+}O_0)^{1+}$ for $x = 7$. This writing emphasizes the changing Cu oxidation and the negative charge accumulation near ${}^pCu$. We note that holes (*5*) are found on O and search for a representation of this charge delocalization. Clearly, there must be two qualitatively different O responsible for two plateaus in a ratio near 2 : 1. ${}^pO$ and ${}^aO$ are the natural choices especially as O in ${}^cCu$ "plane" are part of the insulating charge reservoir. The following is the proposed sequence of events with increasing $x$ in $YBa_2Cu_3O_x$:

$x = 6$. This semiconducting composition can be represented as $(Y^{3+}\ Cu_2^{2+}\ {}^pO_4^{2-})^{1-}(Ba_2^{2+}\ {}^aO_2^{2-})({}^cCu^{1+}O_0)^{1+}$. Accordingly, Ba is attracted to ${}^pO$, and ${}^aO$ to ${}^cCu$. The short ${}^cCu$ ${}^aO$ distance is shown in Fig. 1 as a function of $x$ derived from Ref. (*3*). With increasing $x$, ${}^cCu$ increases from 1+ to 2+ but charge stays localized.

*$x = 6.5$.* Near $x = 0.5$ charge delocalization and rearrangement resulting in $T_c \sim 60$ K occur. On low temperature–low O pressure synthesis (*3*), this transition occurs already near $x = 6.4$ and entails a stepwise decrease in the *c* axis. This change appears also to be reflected in an increasing distance $^{c}$Cu$^{a}$O (Fig. 1) (although the data in Fig. 1 for $x = 6.5$ are for a yet nonsuperconducting material). The rearrangement toward more positive charge near $^{p}$Cu and less positive charge at $^{c}$Cu is also reflected by the decreasing *a* axis (influencing $^{p}$Cu) and increasing *b* axis (primarily influencing $^{c}$Cu). We shall not attempt to quantitatively determine the extent of this charge rearrangement and for simplicity, assume that $^{c}$Cu changes from 2+ to 1+. This is represented as $(Y^{3+}Cu_2^{2+}\ {}^{p}O_3^{2-}\ {}^{p}O^{1-})^0(Ba_2\ {}^{a}O_2^{2-})({}^{c}Cu^{1+}O_{0.5})^0$ showing a formal peroxide state $^{p}O^{1-}$. This means that one hole can flow into four $^{p}$O (it is gratifying that the second charge transfer near $x = 0.75$ occurs with the same stoichiometric proportions namely half a hole for two $^{a}$O). The driving force for this charge rearrangement is obviously the reduction of excess negative charge near $^{p}$Cu. Increasing *x* will now increase the charge on $^{c}$Cu. The $^{c}$Cu system, however, stays localized and does not contribute to $T_c$ so that $T_c$ can stay at a plateau. Near $x = 6.67$, positive charge starts to flow also into $^{a}$O. The process is complete near $x = 0.75$ (see stoichiometric considerations above) and we take this composition as a separate superconducting phase.

*$x = 6.75$.* This is the beginning of the $T_c \sim 90$ K plateau. We assume that charge disproportion has again resulted in $^{c}Cu^{1+}$ and the formation of a formal peroxide now also on $^{a}$O according to $(Y^{3+}\ {}^{p}Cu_2^{2+}\ {}^{p}O_3^{2-}\ {}^{p}O^{1-})^0(Ba_2\ {}^{a}O_{1.5}^{2-}\ {}^{a}O_{0.5}^{1-})^{0.5+}({}^{c}Cu^{1+}O_{0.75})^{0.5-}$. In this range, the $^{p}$Cu $^{a}$O distance shortens on entering the superconducting state (*9*). On increasing *x*, $^{c}$Cu valency increases, but these charges again stay localized.

TABLE I

EXPECTED $T_c$ PLATEAUS IN COMPOUND SERIES SUCH AS $Bi_2Sr_2Ca_{n-1}Cu_nO_x$

| *n* | $^{p}$O/$^{a}$O | Expected $T_c$ (K) plateaus |
|---|---|---|
| 1 | 1 : 1 | 30 and 60 K |
| 2 | 2 : 1 | 60 and 90 K |
| 3 | 3 : 1 | 90 and 120 K |
| 4 | 4 : 1 | 120 and 150 K |

## Discussion

Several experimental facts and predictions follow naturally from a correlation of $T_c$ with $^{p}$O and $^{a}$O, respectively. The numbers of $x = 6.5$ and $x = 6.75$ for the onsets of the plateaus in $T_c$ in $YBa_2Cu_3O_x$ can be naturally understood as a result of the need for a specified number of holes (e.g., one hole per four O) in both cases. This results in one formal peroxide, $(O_2)^{2-}$ per eight O and could possibly give an indication for an actual mechanism of superconductivity involving metallic O by electronic transport of a peroxide-type unit through polarization effects.

From the ratios of four $^{p}$O two $^{a}$O and $T_c \sim 60$ to 90 K, we assign $T_c \sim 30$ K per two O. These ratios change in families such as $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ (Table I) and a generalized prediction can be given for potential maximum and minimum values of $T_c$ (K) of $30\,n + 30$ and $30\,n$, respectively, where *n* is the number of $CuO_2$ planes (not including, e.g., $^{c}$Cu). Experimental data of $T_c$ are given in Table II for a variety of ceramic superconductors. It is seen that experimental $T_c$ either reflect predicted maximum (full $^{p}$O and $^{a}$O involvement) or minimum values ($^{p}$O involvement only). As an example for $Bi_2Ca_{n-1}Sr_2Cu_nO_x$ with $n = 3$, the ratio $^{p}$O/$^{a}$O is 3 : 1 and we expect possible plateaus in $T_c$ of 90 and 120 K. These plateaus could become developed by either changing O

TABLE II

CHARGE POLARIZATIONS AND SUPERCONDUCTING HOLES (ASTERISKS) IN CERAMIC SUPERCONDUCTORS

| Material[a] | $T_c$ (K)[b] |
|---|---|
| $(\mathrm{RCu}_2^{2+}\,{}^{p}\mathrm{O}_4^{*})^{-1}(\mathrm{Ba}_2\,{}^{a}\mathrm{O}_2)(\mathrm{Cu}^{2+}\mathrm{O}_{0.5})^{+1}$ | 60 |
| $(\mathrm{RCu}_2^{2+}\,{}^{p}\mathrm{O}_4^{*})^{-1}(\mathrm{Ba}_2\,{}^{a}\mathrm{O}_2^{*})(\mathrm{Cu}^{3+}\mathrm{O}_1)^{+1}$ | 90 |
| $(\mathrm{RCu}_2^{2+}\,{}^{p}\mathrm{O}_4^{*})^{-1}(\mathrm{Ba}_2\,{}^{a}\mathrm{O}_2^{*})(\mathrm{Cu}^{2.5+}\mathrm{O}_2)^{+1}$ | 80 |
| $(\mathrm{Ca}_0\mathrm{Cu}^{2+}\,{}^{p}\mathrm{O}_2^{*})^{-2}(\mathrm{Sr}_2\,{}^{a}\mathrm{O}_2)(\mathrm{Bi}_2\mathrm{O}_2)^{+2}$ | 20 |
| $(\mathrm{Ca}_1\mathrm{Cu}_2^{2+}\,{}^{p}\mathrm{O}_2^{*})^{-2}(\mathrm{Sr}_2\,{}^{a}\mathrm{O}_2^{*})(\mathrm{Bi}_2\mathrm{O}_2)^{+2}$ | 90 |
| $(\mathrm{Ca}_2\mathrm{Cu}_3^{2+}\,{}^{p}\mathrm{O}_6^{*})^{-2}(\mathrm{Sr}_2\,{}^{a}\mathrm{O}_2^{*})(\mathrm{Bi}_2\mathrm{O}_2)^{+2}$ | 120 |

[a] Asterisks indicate the location of superconducting holes generated by changes in $^{c}$Cu valency or by nonstoichiometry (not represented). Maximum predicted $T$ (K) is $30\,n + 30$. Where this is not reached, $^{a}$O are not involved in superconductivity.

[b] Maximum values reported (e.g., Ref. (*1*)).

content $x$ or cation charge. For reports of higher $T_c$ than given in the above $T_c$ ($n$) relationship, caution concerning phase purity appears in order. However, $T_c \sim 90$ K for $\mathrm{Tl_2Ba_2CuO_6}$ may actually indicate that even the O in the $\mathrm{Tl_2O_2}$ planes can become superconducting and that further steps in $T_c$ through coupling of all planes may be possible. On the other hand, the fact that $n = 4$ in $\mathrm{TlBa_2Ca_{n-1}Cu_nO_x}$ has so far only shown $T_c \sim 122$ K (comparable or slightly lower than for $n = 3$) may suggest an intrinsic saturation or that in this compound, $^{a}$O has not been turned superconducting yet (e.g., due to lack of oxidation). When $^{a}$O also becomes superconducting (e.g., through partial Na substitution for Ca), we would expect $T_c \sim 150$ K on the simple model. With higher $n$, this linear progression in $T_c$ can be assumed to saturate, although considerably higher values should yet be attainable. In this connection, the $n = \infty$ compound $\mathrm{(CaSr)CuO_2}$ with partial substitution (e.g., Na for Ca) appears interesting.

Materials with $n = 1$ also show a tendency to exclusion of $^{a}$O in superconductivity ($T_c = 30$ rather than 60 K). An exception is $\mathrm{(Tl,Bi)Sr_2CuO_5}$ with $T_c \sim 50$ K. However, $\mathrm{Bi_2Sr_2CuO_x}$ has only $T_c \sim 20$ K. Also, $\mathrm{(LaSr)_2CuO_4}$, while not fully comparable structurally, has $T_c \sim 30$ K. In this respect, it is interesting to note that $\mathrm{(KBa)BiO_3}$ has $T_c \sim 30$ K. This appears to indicate that O in the $\mathrm{BiO_2}$ plane has become fully superconducting in analogy with $n = 1$ phases such as $\mathrm{Bi_2Sr_2CuO_x}$. $\mathrm{Ba(PbBi)O_3}$ has a lower $T_c$ (14 K) because of the disruption of the relevant plane through disordered substitution.

We have in the above not attempted to arrive at a quantitative determination of charge transfer. Such a determination may be possible in an indirect way. Indications exist (*10*) that $^{p}$Cu is formally 2.25 + in $n = 2$ materials such as $\mathrm{Bi_2Sr_2CaCu_2O_x}$. As these materials can have $T_c \sim 90$ K, both $^{a}$O and $^{p}$O must superconduct. The 0.5 holes have, therefore, to be distributed over 6 O. This indicates one hole per 12 O rather than 4 O as assumed above. This also alters the assumed valencies on $^{c}$Cu in $\mathrm{YBa_2Cu_3O_x}$, but does not change the general ideas.

The location of $^{a}$O relative to $^{p}$Cu appears to be of importance concerning the potential for involving $^{a}$O in superconductivity. In this respect, we note that $\mathrm{LaBa_2Cu_3O_x}$ can easily be obtained with $T_c \sim 60$ K, but it is difficult to obtain (*4*) the $T_c \sim 90$ K phase even though $x$ can be near 7. We assign this difficulty to structural peculiarities in the location of $^{a}$O. Either the relative distances are unsuitable or partial LaBa substitutions near $^{a}$O produce sufficient disorder in the positions to preclude superconductivity on this site. Strong pressure dependencies of $T_c$ can be anticipated in regions where $^{a}$O is electronically and structurally poised to become superconducting.

An important question concerning valencies is the one of limiting O uptake. For $\mathrm{YBa_2Cu_3O_x}$, pressure-composition ($p$, $x$) isotherms show strong saturation near $x = 7$. If this were only reflecting a structural argument, then materials such as (Y Ca) $\mathrm{Ba_2Cu_3O_x}$ should also show (*4, 9*) limiting $x$ near 7. Experimentally, however, $x < 7$, indicating that electron count determines $x$. For $Y_{0.5}Na_{0.5}Ba_2Cu_3O_{6.5}$ (*4*), or a fictitious $CaBa_2Cu_3O_x$ maximum $x = 6.5$. In representation with variable Cu valency, this is $(Ca^{2+}Cu_2^{2+}O_4^*)^{2-}(Ba_2O_2^*)(^cCu^{3+}O_{0.5})^{2+}$ where the asterisks indicate hole formation potential. This shows that the condition for valencies of 2+ for $^p$Cu and 3+ for $^c$Cu can be used to formally determine maximum $x$. It is possible that this fact represents a more fundamental aspect of charge delocalization involving $^cCu^{3+}$ in temporal charge fluctuations to $^p$O and $^a$O.

## Conclusion

From spectroscopic evidence, we concude that superconducting holes reside primarily on O. A natural correlation for $YBa_2Cu_3O_x$ is the one of holes on plane O to be responsible for $T_c \sim 60$ K. When holes penetrate to apical oxygens, $T_c \sim 90$ K. This can be generalized to other known superconductors and leads to the expectation of different $T_c$ plateaus depending on the ratio of $^p$O/$^a$O and their degree of oxidation. In cases where the oxygen content is fixed, these plateaus will have to be developed through partial substitutions with metals of different valencies. As evidence for $^p$O $^a$O involvement, we take the comparable number of holes per atom for the two species (in the relation of 2 : 1 as given by stoichiometry in $YBa_2Cu_3O_x$), the relative magnitude of the two $T_c$ plateaus, and the motion of $^a$O relative to $^c$Cu with $x$. The model involving apical O extends the idea of charge fluctuations from Cu, where no straightforward signs for $Cu^{3+}$ are reported, to the O system. This naturally allows explanation of stable states ($T_c$ plateaus) with $x$ involving $^p$O and $^a$O. If one involves the two Cu with individual contributions to superconductivity, the existence of plateaus cannot be easily explained. If only $^p$Cu is considered, there is no obvious way to explain two electronically distinct states resulting in two $T_c$ plateaus.

## References

*1.* A. W. Sleight, *Science* **242,** 1519 (1988).
*2.* H. Oesterreicher, *J. Solid State Chem.* **76,** 229 (1988).
*3.* R. J. Cava *et al., Phys. C 156,* 523 (1988).
*4.* H. Oesterreicher *et al., Mater. Res. Bull.* **23,** 1327 (1988).
*5.* T. Takahashi *et al., Nature (London)* **334,** 691 (1988).
*6.* H. You *et al., Phys. Rev.* **13,** 9213 (1988).
*7.* Y. Tokura *et al., Phys. Rev.* **13,** 7156 (1988).
*8.* A. Manthiram *et al., J. Solid State Chem.* **73,** 278 (1988).
*9.* W. Schafer *et al., Mater. Res. Bull.* **23,** 1439 (1988).
*10.* H. Oesterreicher *et al., Mater. Lett.* **6,** 254 (1988).