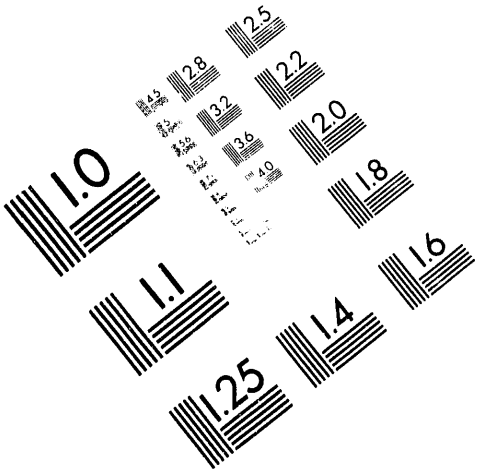

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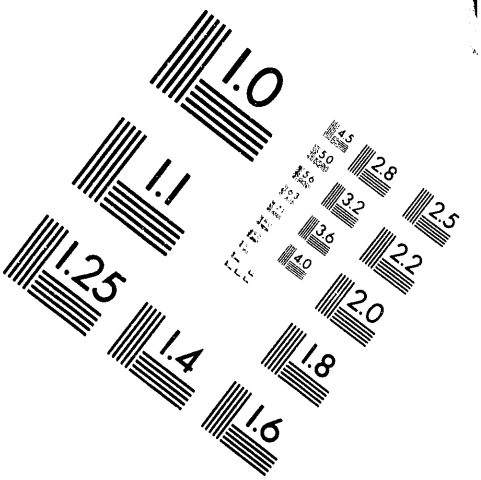

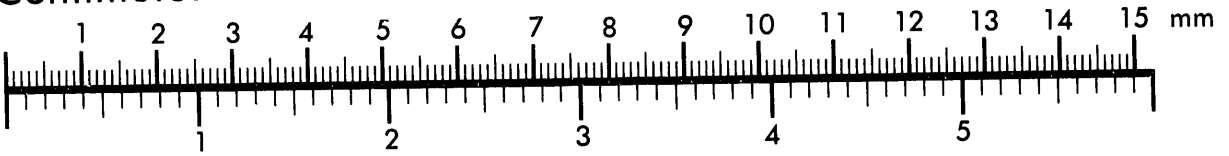

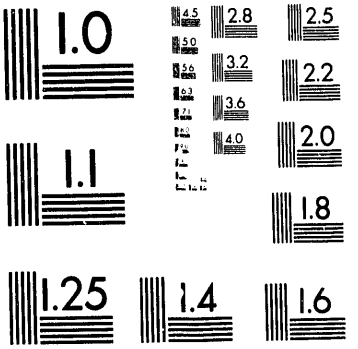

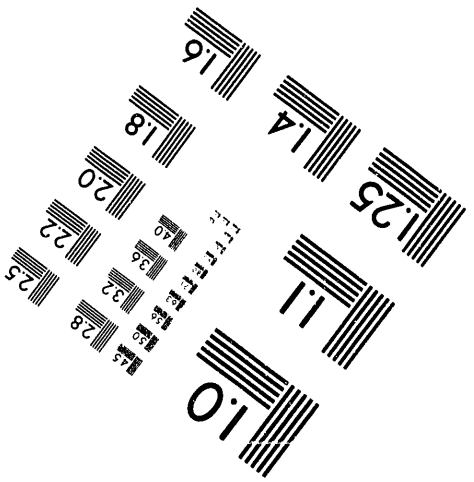

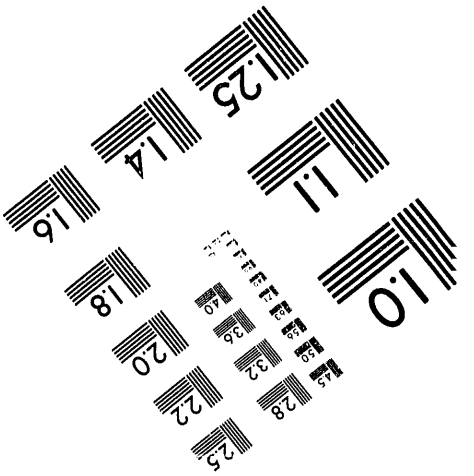

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# ROLES OF OXYGEN DEFECTS IN COPPER-OXIDE SUPERCONDUCTORS

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## ABSTRACT

Oxygen vacancy and interstitial defects can have a profound effect on the superconducting properties of copper-oxide compounds. Recent work on compounds such as $La_2CuO_{4+x}$ and $HgBa_2CuO_{4+x}$ has provided new insight into the role of interstitial oxygen defects as a doping mechanism. Studies of $(La,Sr,Ca)_3Cu_2O_{6+x}$ with various metal compositions and metal-site ordering show that interstitial oxygen defects that form between the $CuO_2$ layers in this structure systematically lower $T_c$ and eventually destroy superconductivity. However, oxygen vacancies in the $CuO_2$ planes have surprisingly little effect at concentrations below 3%. The infinite-layer compounds, $ACuO_2$, where A=La, Sr, Ca, Nd, etc., in solid-solution combinations, offer a very similar environment for the formation of interstitial oxygen defects between the $CuO_2$ planes. However, neutron diffraction experiments on $Sr_{0.9}La_{0.1}CuO_2$ ($T_c$=42K) have not found any interstitial oxygen.

## INTRODUCTION

The important role of defects in controlling the superconducting properties of copper-oxide compounds has been discussed in several previous papers. In this paper we focus attention on recent results that provide additional insight into the effects of oxygen interstitial defects and oxygen vacancies in the $CuO_2$ planes, with some comment on the way in which metal-site ordering influences the formation of the oxygen defects.

## ELECTROCHEMICALLY OXIDIZED $La_2CuO_{4+x}$

Several authors have recently shown that electrochemical methods at room temperature can be used to achieve higher oxygen concentrations in $La_2CuO_{4+x}$ than were ever achieved by high-oxygen-pressure techniques at high temperature.[3,4] This has allowed for the first time the synthesis of samples with oxygen contents beyond the well-known miscibility gap.[5] We have recently reported neutron diffraction studies of the structure for single-phase samples with x=0.08 and 0.12.[6] The basic (average) structure is orthorhombic space group Fmmm, which has no "tilts" of the $CuO_6$ octahedra, with the excess oxygen being located in the $La_2O_2$ layer at the (1/4,1/4,1/4) position. However, a very large supercell, which has not yet been solved, is present, suggesting a complex ordering of the interstitial oxygen defects and, perhaps, associated displacements of oxygen atoms or tilts of the octahedra. Until the supercell is solved, the details of this ordering will not be understood. One of the interesting things learned from the electrochemically oxidized samples is that $T_c$ continues to increase with increasing oxygen content reaching 44K for the highest oxygen content yet achieved (x=0.12). If the excess-oxygen defects were contributing two holes per oxygen atom, this concentration would be well into the overdoped regime. This observation suggests that the oxygen (or at least part of it) may be incorporated in a way other than isolated $O^{2-}$ interstitial defects. Chaillout et al. have previously suggested the existence of short O-O bonds involving the defect oxygen atom.[7] More recently, a complete solution of the complex supercell structure of the related compound $La_2NiO_{4.25}$ has shown that short O-O bonds, requiring a

charge state other than $O^{2-}$, is part of the defect ordering scheme in that compound.[8] A similar circumstance may exist in $La_2CuO_{4+x}$.

## INTERSTITIAL OXYGEN DEFECTS IN $HgBa_2CuO_{4+x}$

Interstitial oxygen defects are also the doping mechanism in the newly discovered[9] single-layer compound $HgBa_2CuO_{4+x}$ shown in Fig. 1. In a recent neutron powder diffraction study of this compound we have shown that $T_c$=95K (onset of diamagnetism) is achieved when x=0.06.[10] Removing this oxygen lowers the $T_c$ to 59K for x=0.01. This behavior is consistent with each interstitial oxygen defect (O3 in Fig. 1) contributing two holes. The defect is located in the plane of the Hg atoms, but is not bonded to Hg, since the bonding to apical oxygen atoms above and below (O2 in Fig. 1) satisfies the preferred two-fold coordination of Hg. It is interesting to note that a second oxygen defect (O4) forms in this compound. A small amount of extra oxygen is apparently incorporated at the O4 site (somewhat analogous to the chain oxygen site in 123 compounds) because Cu substitutes for some (~8%) of the Hg at the Hg site.

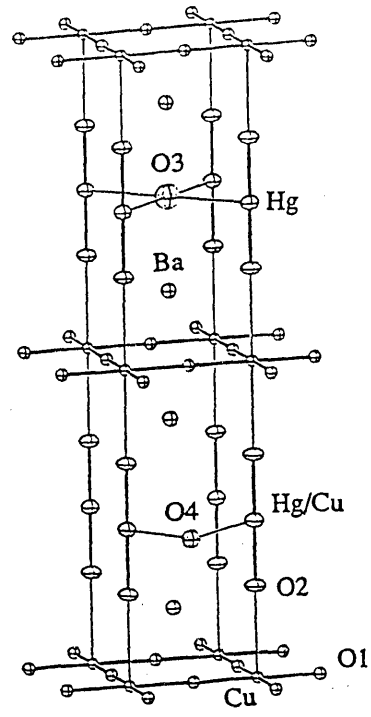


Fig. 1. Structure of the 95K superconductor $HgBa_2CuO_{4+x}$. O3 and O4 are partially occupied oxygen defect sites.

## OXYGEN DEFECTS IN TWO-LAYER $(La,Sr,Ca)_3Cu_2O_{6+x}$ COMPOUNDS

The heavily studied two-layer compounds $(La,Sr,Ca)_3Cu_2O_{6+x}$ offer a challenging but very interesting example of the roles of both oxygen interstitial and vacancy defects. We have recently completed a study of these compounds in which the defect concentrations were varied in a systematic way.[11] The incorporation of excess oxygen at a site between the $CuO_2$ layers and the formation of oxygen vacancies within the $CuO_2$ layers are both influenced by the metal composition and metal site ordering (which varies with the synthesis conditions). The spacing between the $CuO_2$ layers ($d_{Cu-Cu}$ in Fig. 2) is controlled by the average size of the metal ions on the site between the layers. When the larger La and Sr ions occupy this site, the spacing increases. The amount of defect oxygen (O3) between the layers increases sharply when this spacing exceeds 3.5 Å, as shown in Fig. 3. The incorporation of oxygen at this site systematically lowers $T_c$ as shown in Fig. 4, with superconductivity being destroyed when this concentration exceeds about 0.15 oxygen atoms per formula unit. Surprisingly, oxygen vacancy concentrations in the $CuO_2$ layers up to about 3% appear to have little effect on superconductivity. (No samples with larger vacancy concentrations were studied.)

## ABSENCE OF OXYGEN DEFECTS IN INFINITE-LAYER $Sr_{0.9}La_{0.1}CuO_2$ ($T_c$=42K)

The superconducting infinite-layer compounds are of particular interest because of their simple structures and the speculation that these compounds may achieve the highest $T_c$'s

possible for layered copper oxides if properly doped. In light of what we know about oxygen defects in other copper-oxide superconductors, it is important to determine whether oxygen interstitial or vacancy defects form in these compounds. Neutron diffraction offers a sensitive technique for probing this aspect of the structures, but the small sample size (typically <100 mg) is a serious challenge. We have recently developed techniques for lowering the neutron background enough to obtain high quality diffraction data from small (<50 mg) samples of this material and have reported the first neutron powder diffraction study of the electron-doped infinite-layer compound $Sr_{0.9}La_{0.1}CuO_2$ ($T_c$=42K).[12] The raw time-of-flight diffraction data and Rietveld refinement profile are shown in Fig. 5. Within an experimental uncertainty of 1%, we found no oxygen vacancies in the $CuO_2$ layers and no interstitial oxygen between the layers. The latter result is consistent with our finding (in the two-layer compound discussed above) that significant oxygen is incorporated between the $CuO_2$ layers only when the spacing between CuO2 layers, $d_{Cu-Cu}$, exceeds 3.5 Å, since for superconducting $Sr_{0.9}La_{0.1}CuO_2$, $d_{Cu-Cu}$=3.4 Å.

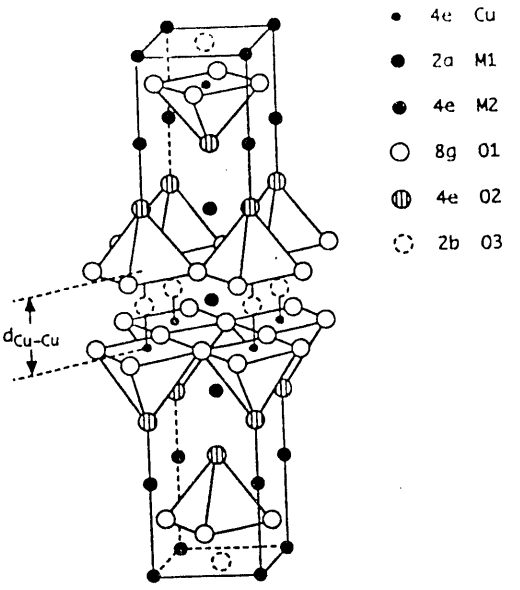


Fig. 2. Structure of the two-layer compound $(La,Sr,Ca)_3Cu_2O_{6+x}$ showing the oxygen defect site, O3, that is occupied when the spacing between $CuO_2$ layers, $d_{Cu-Cu}$, exceeds 3.5 Å. Metal sites M1 and M2 are occupied by La, Sr, and Ca.


ACKNOWLEDGMENTS

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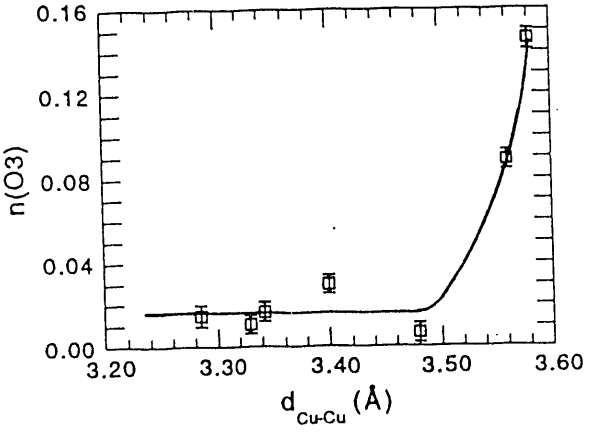


Fig. 3. Number of oxygen defects (per formula unit) between the $CuO_2$ layers of $(La,Sr,Ca)_3Cu_2O_{6+x}$ as a function of the spacing between layers.

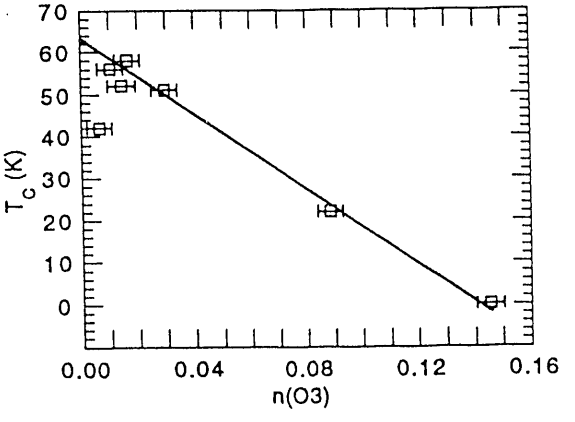


Fig. 4. $T_c$ of $(La,Sr,Ca)_3Cu_2O_{6+x}$ as a function of the number of oxygen defects between the $CuO_2$ layers.

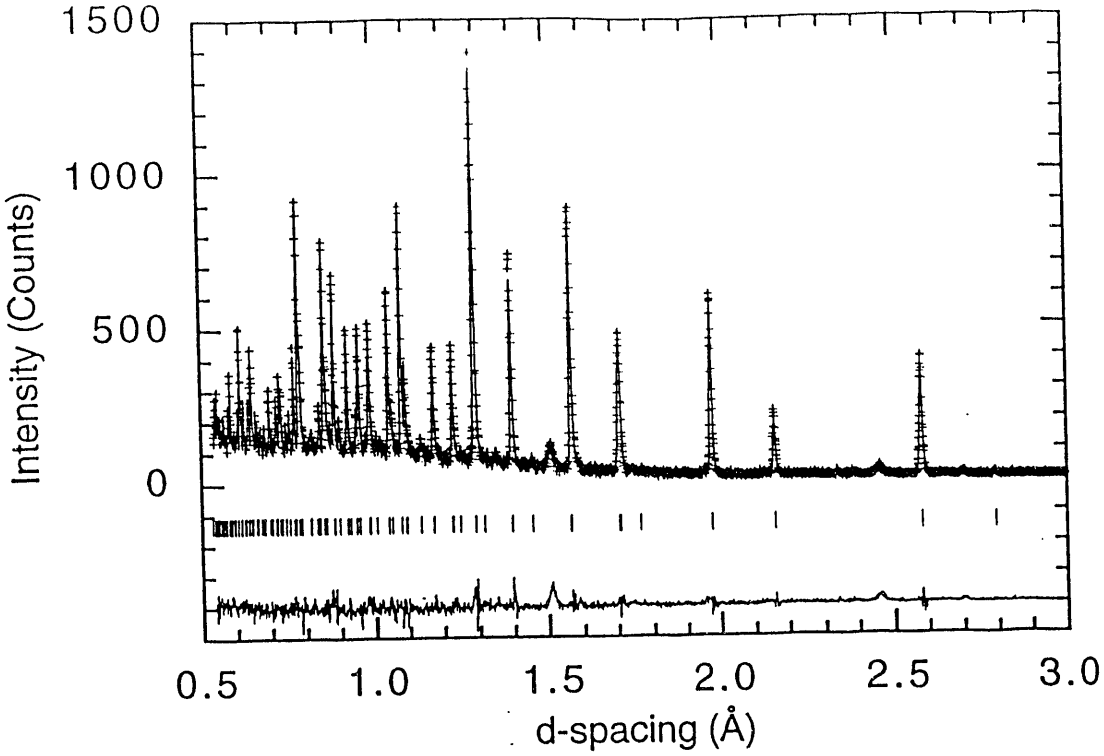


Fig. 5. Rietveld refinement profile for $Sr_{0.9}La_{0.1}CuO_2$. Data were collected from an 82 mg sample for 12 h on the Special Environment Powder Diffractometer at Argonne's Intense Pulsed Neutron Source. Plus marks (+) are the raw time-of-flight diffraction data including background. The solid line is the calculated profile. Tick marks below the profile mark the positions of allowed reflections in the tetragonal P4/mmm space group. A difference curve (observed minus calculated) is plotted at the bottom.

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