

Structural Relationships in High Temperature Superconductors

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The recent discovery of two types of metallic copper oxide compounds which are superconducting to above 90K has renewed interest in the search for new high temperature superconducting materials. It is significant that both classes of compounds, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are intimately related to the extensively studied perovskite family. Both compounds contain highly oxidized, covalently bonded Cu-O sublattices, however, they differ in geometry. In this paper we discuss the relationship of these features to the superconducting properties.

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$

Superconductivity above 30K was first discovered in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ with the K_2NiF_4 tetragonal structure^{1-4]}. Subsequent work revealed that T_c could be raised to 37K by replacement of Ba by Sr^{5]}. The undoped La_2CuO_4 compound, which forms in an orthorhombically distorted variant of the K_2NiF_4 structure is non-metallic at low temperatures and shows no superconductivity. Recently it has been shown that in the stoichiometric material, the Cu ions order antiferromagnetically^{6-8]}. There are also reports that this compound can be made superconducting by special post-synthesis procedures^{9]}, however the superconductivity might not be bulk and the reason for its existence is not yet understood. As Sr is substituted for La, superconductivity appears with T_c increasing until $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-y}$. The basic structure of tetragonal $\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$ (M=Sr, Ba) is shown in Figure 1^{10]}, however, at low temperatures there is evidence for a slight orthorhombic distortion^{11]}. This distortion has little effect on the structural properties we will be discussing below. The most prominent feature in this structure is the presence of two-dimensional (2D) Cu-O planes with short (1.888 Å) distances within the plane. The Cu atoms are octahedrally coordinated with two relatively distant oxygen atoms above and below the planes (2.416 Å). All of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ compounds have very low carrier concentrations^{12,13]}, consistent with

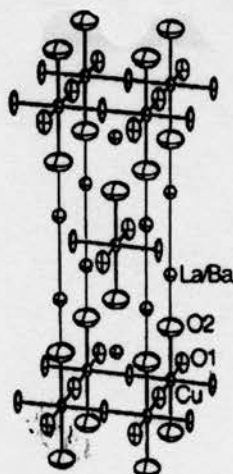


Figure 1. The structure of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$. The Sr-substituted compound has the same structure (ref. 10).

each Sr atom producing a single hole. From a chemical standpoint, the addition of Sr can be considered as increasing the formal oxidation state of the copper. Assuming O^{2-} , La^{+3} and Sr^{+2} , and a composition of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ for the compound with the maximum T_c , the calculated formal charge state of Cu is +2.15. Partial substitution for the Cu atoms in this structure rapidly depresses T_c to 0K within a few percent, while magnetic rare earth substitution for La leads to a slow decrease in T_c ^{14]}. Full substitution of rare earth ions is not possible in this compound because of a structural phase transition which completely destroys superconductivity^{15]}.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

The current confirmed record-holder for T_c ($\approx 90\text{K}$) is $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, which was discovered as a minority phase in attempts to raise the T_c of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ by replacing La with Y^{16]}. Subsequently, the single phase composition was found to be $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ^{17-19]} with the orthorhombic structure shown in Figure 2^{20]}. This structure is composed of dimpled 2D Cu-O planes and one-dimensional (1D) Cu-O chains separated by fairly large distances. The Cu-O bond lengths are 1.928 Å and 1.962 Å within the 2D planes and 1.943 Å along the 1D chains. Furthermore, the Cu1-O4 distance above and below the chains is quite short (1.850 Å). Various neutron diffraction studies find the exact composition to be $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$, corresponding to a formal charge state of +2.23 for Cu^{20-23]}. At high temperatures, this compound undergoes a phase transition to a tetragonal structure (Figure 3)^{24,25]}. In-situ

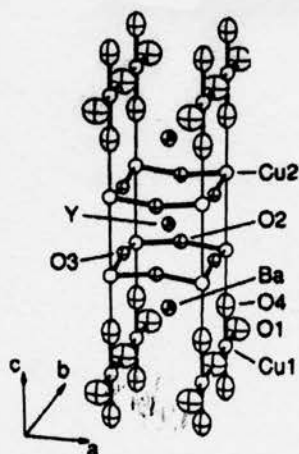


Figure 2. The orthorhombic structure of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (ref. 20).

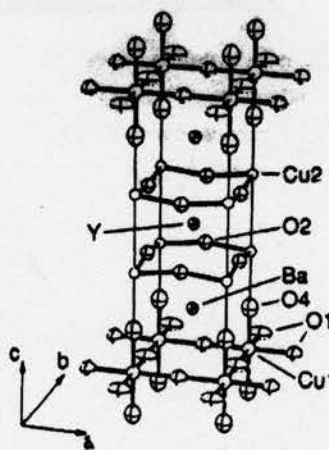


Figure 3. The high-temperature, non-superconducting tetragonal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (ref. 26).

neutron diffraction shows that as the temperature is increased, the oxygens in the 1D chains disorder into the formerly vacant positions along the a -axis²⁶. Figure 4 shows the site occupation of oxygen in the basal plane as a function of temperature under 100% O_2 . At 750°C, site occupations become equal and the compound becomes tetragonal. The total oxygen stoichiometry of this compound depends on temperature and oxygen partial

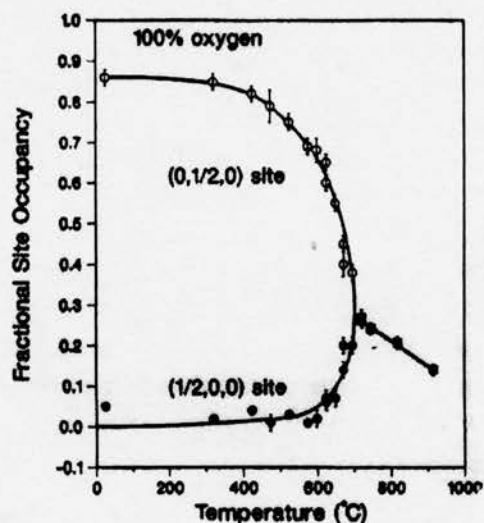


Figure 4. Oxygen site occupancy as a function of temperature in the basal plane of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ under 100% oxygen (ref. 26).

pressure as shown in Figure 5. The temperature at which the structural phase transition occurs is indicated by the vertical lines and is found to correspond to an oxygen content of 6.5, independent of oxygen partial pressure. It should be noted that this stoichiometry corresponds to a formal charge state of +2.00 for Cu. Studies of quenched samples have shown that T_c decreases monotonically to zero at the phase transition²⁷.

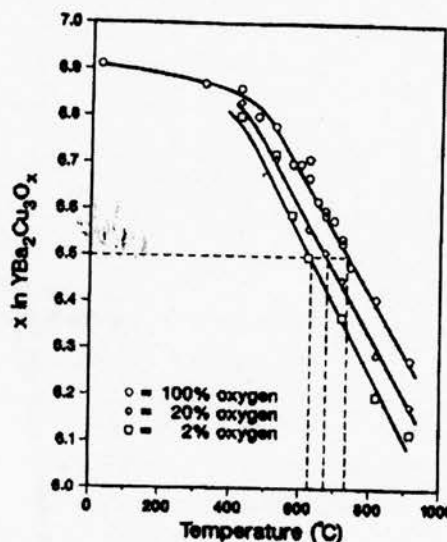


Figure 5. Total oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_x$ as a function of temperature for varying partial pressures of oxygen. The vertical dashed lines mark the temperature of the orthorhombic-to-tetragonal phase transition (ref. 26).

Substitution of Y by trivalent rare earth elements does not affect T_c despite the rare earth magnetic moments being introduced into the structure^{28,29}. Of the three rare earths which have stable tetravalent states (Ce, Pr and Tb), only Pr can be substituted for Y in this compound³⁰. Figure 6 shows the temperature dependent relative resistivity for various concentrations of Pr in $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. If Pr enters as a tetravalent ion, the observed transition from metallic to semiconducting behavior could be understood as a reduction of the formal charge state of Cu to below +2.00.

Structural Considerations and Superconductivity

The origin of superconductivity in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ compounds is clearly in the 2D Cu-O planes, while there is some question as to whether the 1D chains or the nearly 2D planes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are more important for superconductivity. It is surprising that the addition of 1D chains more than doubles the superconducting transition temperature. Some insight can be gained by considering the results of magnetic rare earth substitution into both these structures. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, the magnetic ion lies

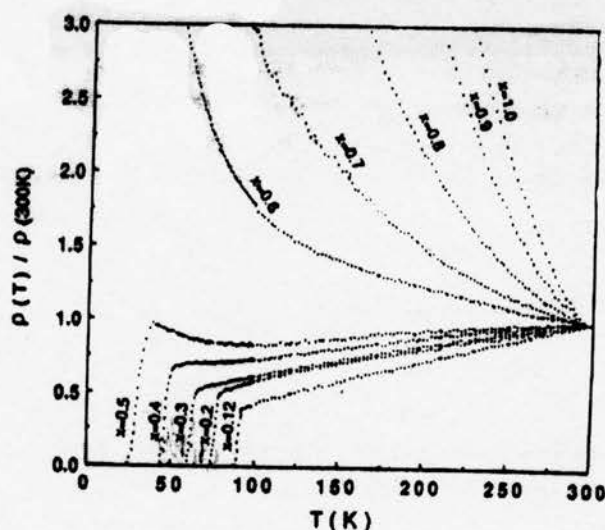


Figure 6. Relative resistivity as a function of temperature for compounds in the series $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (ref. 30).

adjacent to the planes carrying the superconductivity (see Figure 1, La/Ba positions) and depresses T_c . On the other hand, the $YBa_2Cu_3O_{7-\delta}$ structure is quite insensitive to magnetic rare earth ions whose location is adjacent to the 2D planes but far from the 1D chains (see Figure 2, Y positions). This result seems to indicate that superconductivity may reside in the 1D chains. However, it is also possible that the chains may only serve to stabilize a structure in which two Cu-O 2D planes are much closer together (3.50 Å) than the equally spaced planes in $La_{2-x}Sr_xCuO_{4-y}$ (6.65 Å). The effect of dimensionality on superconductivity in these materials is far from being understood and will require a great deal of additional experimental and theoretical effort.

Superficially, one of the most striking differences in the two compounds is that $La_{2-x}Sr_xCuO_{4-y}$ is basically a solid solution, with La and Sr sharing the same crystallographic sublattice. In contrast, $YBa_2Cu_3O_{7-\delta}$ is a stoichiometric compound with independent Y and Ba sublattices. When one considers the defect nature of these compounds, however, they are electronically quite similar, being low carrier density "doped semiconductors". Both La_2CuO_4 and $YBa_2Cu_3O_{6.5}$, which contain only divalent copper, exhibit semiconducting behavior at low temperatures^{10]}. In both these materials, metallic-like behavior and superconductivity occur when the copper is oxidized to greater than a divalent state. In $La_{2-x}Sr_xCuO_{4-y}$ this is accomplished by doping with divalent Sr while in $YBa_2Cu_3O_{7-\delta}$, the same effect is obtained through increasing the oxygen content. Because of the strong covalent nature of the Cu-O

sublattices in these materials, it may be inappropriate to consider formal oxidation states of the copper. Indeed, while these compounds are oxidized in a chemical sense, the holes introduced by doping are delocalized over the entire Cu-O sublattices. In light of this "doped semiconductor" picture, it is not surprising that defects play a major role in determining the electrical, magnetic and superconducting properties of these compounds. A good example is the "unintentionally doped" La_2CuO_4 compound which exhibits a wide range of magnetic and superconducting properties caused by the incorporation of as yet unidentified electrically active defects.

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