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Key Insights from Structural Studies of High-Temperature Superconductors: Is There a Path to Higher T_c?

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Abstract: Structural studies have allowed the development of a model for the "ideal" high-temperature superconductor. For a given compound, the maximum T_c is traditionally achieved by using a chemical variable to adjust the carrier concentration to the optimum value. When comparing different compounds at their optimum doping, the highest T_c is observed for compounds with flat CuO_2 planes. T_c can also be enhanced if the charge reservoir region, or blocking layer, is metallic. In general, these three criteria cannot simultaneously be met by adjusting a single chemical/structural variable. Additionally, recent work on $HgBa_2CuO_{4+x}$ and 123 compounds as a function of doping suggest that electronically-driven structural distortions may hinder attempts to produce higher T_c's by chemical substitutions. In spite of these challenges, the ideal high-T_c compound has not yet been discovered and the search should continue.

Keywords: Crystal structure, Maximum T_c, Doping, Electronic Structure, Electronically-driven structural instability

INTRODUCTION

Although over fifty distinct copper-oxide superconductors have been discovered since 1986 [1], the superconducting transition temperature, T_c, (at ambient pressure) has not been raised above 135 K, which was achieved in the three-layer $HgBa_2Ca_2Cu_3O_{8+x}$ compound in 1993.[2] Nevertheless, the wide variety of structural features manifest by these compounds has led to a consensus concerning what chemical/structural features give rise to the highest T_c. In this paper, I review these conclusions and discuss the challenge of finding new compounds with higher T_c's.

OPTIMUM DOPING

The first critical insight from structural studies was that chemical modification of the charge reservoir layer (also called the blocking layer) could be used to create carriers in the metallic CuO_2 conduction layer which is responsible for the superconductivity. Perhaps the most convincing demonstration of this principle was that the bond valence sum for the Cu atoms in the CuO_2 planes in $YBa_2Cu_3O_{6+x}$ scaled with the oxygen content in the CuO_x chains in the charge reservoir layer.[3] This bond valence sum is an estimate of the charge at the plane Cu site calculated from the lengths of the Cu-O bonds around this site. This concept of creating carriers in the CuO_2 planes through chemical modification of the charge reservoir layer came to be known as the charge transfer model.

Consistent with this hypothesis, it was found that a variety of defects could be used in the charge reservoir layer to control the concentration of charge carriers. For example, in the

insulating La_2CuO_4 compound, superconductivity can be created by substitution of a 2+ cation (e.g., Ba, Sr, or Ca) on the La^{3+} site or by insertion of interstitial oxygen defects in the La_2O_2 charge reservoir layer.[4] However, the relationship between the charge transfer and the defect chemistry can be rather complex, such as the case where defect ordering in the chain region of $YBa_2Cu_3O_{6+x}$, at constant oxygen content, dramatically affects the charge transfer and the T_c.[5]

DEFECTS IN THE CuO_2 LAYERS

Whereas defects in the charge reservoir layer may be required to achieve the desired carrier concentration, defects in or near the CuO_2 layers are clearly detrimental to superconductivity. This is especially true for the substitution of metal atoms on the plane Cu site.[6] Small concentrations of such defects destroy superconductivity. $(La,Sr,Ca)_3Cu_2O_{6+x}$ is a particularly interesting system for the study of defects near the CuO_2 layers. This is the two-layer compound in the series beginning with La_2CuO_4. When first discovered, $La_2SrCu_2O_6$ was found to be metallic, but, mysteriously, not superconducting. It was subsequently shown that substitution of a small Ca cation at the metal site between the two CuO_2 planes (analogous to the Y site in $YBa_2Cu_3O_7$) produced superconductivity by reducing the dimensions of the structure in this region and eliminating the formation of an interstitial oxygen defect within the double CuO_2 layer.[7] The formation of defects in or near the CuO_2 layers may explain why some metallic layered copper-oxide compounds do not exhibit superconductivity.

OPTIMUM STRUCTURE FOR HIGH T_c

The observation of a wide range of maximum T_c's in the various copper-oxide superconductors, after carrier concentration is optimized and detrimental defects are eliminated in or near the CuO_2 layers, argues that there is an optimum structure for achieving the highest T_c. Conclusions about the features of this optimum structure come from comparing different compounds. The highest T_c's are observed for compounds with flat CuO_2 planes. The $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ compounds satisfy this criteria. The n=1, 2, and 3 members of this series exhibit the highest T_c's reported for any one-, two-, or three-layer compounds (Table 1). The important feature of the structures of these three compounds is that the strong bonding of the apical oxygen atom to Hg results in a weak, and unusually long, bond of this oxygen atom to the plane Cu atom. This long apical Cu-O bond reduces the repulsion between the apical oxygen atom and the oxygen atoms in the CuO_2 plane, allowing flat CuO_2 planes.

Table 1. Buckling angles of the CuO_2 planes (Cu-O-Cu) and copper-oxygen apical bond lengths (Cu-O) for $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ compounds. Numbers in parentheses are standard deviations of the last significant digit. (from Refs. 8, 9, 10)

No. of layers, n	T_c (K)	Cu-O-Cu (°)	Cu-O (Å)
1	95	180	2.780(1)
2	126	179.4(2)	2.775(3)
3	135	178.4(4)	2.741(6)

The importance of the buckling angle of the CuO_2 planes can be seen by comparing the T_c's and buckling angles for several compounds, as shown in Fig. 1.[11] Only compounds with two CuO_2 layers are shown in this figure because the most accurate structural data are available for these compounds. The same behavior is observed for three-

layer compounds, but with fewer data. (For one-layer compounds, the occurrence of different structural distortions, such as the coordinated tilting of CuO_6 octahedra in La_2CuO_4, make such a comparison difficult.) For the two-layer compounds with insulating charge reservoir layers ($La_2CaCu_2O_6$, Tl-1212, Bi-2212, Tl-2212, and Hg-1212), the correspondence between T_c and CuO_2 plane buckling is remarkable. Flat planes lead to higher T_c's. A few degrees of buckling lowers T_c substantially. The $HgBa_2CaCu_2O_{6+x}$ compound has a buckling angle of 179.4°, implying that a small increase in T_c (perhaps 10 K) would be achieved if the plane could be made perfectly flat.

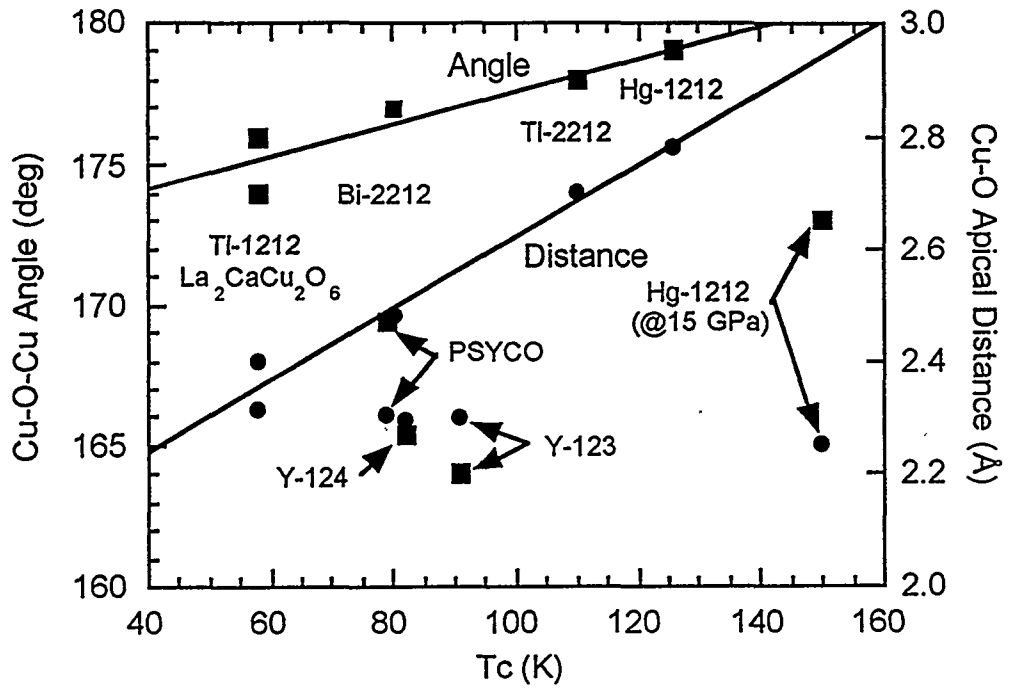

Fig. 1. Relationship between T_c, the Cu-O-Cu bucking angle of the CuO_2 planes (square symbols), and the Cu-O apical bond distance (round symbols) for compounds with two CuO_2 layers.

A number of studies where the buckling angle has been varied while holding the doping level constant have confirmed this relationship between T_c and buckling angle. The simplest and most direct confirmation comes from the studies of $La_{2-x}Sr_xCuO_4$ vs. pressure by Yamada and Ido.[12] Pressure reduces the buckling angle of the CuO_2 planes in the orthorhombic structure until a continuous transformation to a tetragonal structure with flat planes occurs. T_c increases linearly with pressure until the planes become flat and then remains constant with pressure. Experiments by Dabrowski et al., where the buckling angle is varied through chemical substitution in $La_{2-x}M_xCuO_4$ (M=Nd,Ca,Sr) lead to the same conclusion.[13] The same behavior is observed in other high-T_c compounds, such as the 123 materials, and there are several electronic structure calculations that provide an explanation in terms of how buckling affects the electronic density of states at the Fermi energy. This topic is reviewed in Ref. 14.

A recent report of the effect of structural disorder on T_c may also be explained in terms of the effects of disorder on local buckling angle. Attfield et al. [15] showed that T_c

decreases systematically with increasing variance of the size of the charge reservoir cation in $Ln_{1.85}M_{0.15}CuO_4$, where the combination of Ln (La or Nd) and M (Sr, Ba, or Ca) is chosen to conserve the doping level while introducing structural disorder because of the different sizes of the cations. They offered no fundamental explanation for why the resulting lattice strains lower T_c. I suggest that the suppression of T_c is caused by increases in the buckling angle (which was not measured) in the local structure resulting from the strain.

Fig. 1 also illustrates the behavior of several two-layer compounds that violate the expected relationship between T_c and buckling angle. These are all compounds where the charge reservoir layer is metallic. In this context, the concept of a metallic charge reservoir layer means that there are bands associated with this region of the structure that lie near the Fermi energy and, thus, contribute to the electronic properties. This is true for $YBa_2Cu_3O_{6+x}$ (Y-123) if the CuO_x chains are fully populated with oxygen ($x \approx 1$) and for $YBa_2Cu_4O_8$ (Y-124) and $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ (PSYCCO), all of which have Cu in the charge reservoir layer. This observation suggests that metallization of the charge reservoir layer, which reduces the anisotropy in the normal-state conductivity and increases the c-axis coupling between CuO_2 layers, can increase T_c significantly. The most striking illustration of this phenomena is the behavior of the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ compounds at high pressure. For most high-T_c compounds, pressure is thought to increase T_c by promoting charge transfer; and, therefore, the effects of pressure are small for the composition that is optimally doped.[16] In contrast, pressure substantially raises the T_c's of the optimally-doped n=1, 2, and 3 $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ compounds (by 30 K or more in each case).[17] This has been explained by band structure calculations based on the pressure-induced changes in the structures.[18] Pressure moves a band associated with the HgO_x layer to the Fermi energy; i.e., pressure metallizes the charge reservoir layer and this contributes to an increased T_c in spite of the CuO_2 plane buckling that results from the structural compression. The similarity to the other compounds with metallic charge reservoir layers is striking. As shown in Fig. 1, when pressure is applied to the Hg-1212 compound, which originally has an insulating blocking layer and obeys the expected behavior for those compounds, it transforms to a compound with a metallic blocking layer and has a higher T_c in spite of the increased plane buckling. The ideal compound with flat CuO_2 planes and a metallic charge reservoir layer has not yet been discovered.

ELECTRONIC BARRIER TO ACHIEVING HIGHER T_c

These observations for the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ compounds provide critical insight into the challenge that must be met to increase the (ambient pressure) T_c of layered copper-oxide compounds beyond the present record of 135 K. One must achieve a structure with flat CuO_2 planes; the chemistry of the charge reservoir layer must be adjusted to achieve optimal doping of the CuO_2 planes; and the charge reservoir layer must also be metallic. In terms of the electronic structure, I assume that the latter two criteria mean that bands associated with the CuO_2 planes and the charge reservoir layer must simultaneously be at the Fermi energy. These criteria cannot, a priori, simultaneously be achieved by adjusting a single chemical variable. Hence, it is clear why both chemical doping and pressure must be used to achieve the highest T_c in the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ compounds -- two variables are needed to adjust two bands to lie at the Fermi energy.

Recent work on the $HgBa_2CuO_{4+x}$ compound suggests that electronically-driven structural distortions may increase the difficulty of making the ideal high-T_c material. Fig. 2

shows the T_c and unit cell volume of $HgBa_2CuO_{4+x}$ as a function of the internal structural parameter [z(Ba)-z(O2)].[19] This structural parameter, which generally decreases with increasing oxygen content, is a measure of the charge transfer as oxygen is added to the compound. At the maximum T_c, as the material passes from the under-doped to the over-doped state, there is a region where T_c remains constant and the unit cell volume increases while oxygen is added. This anomalous increase in the unit cell volume changes the structure so that the band associated with the Hg-containing charge reservoir layer does not lie at the Fermi energy; i.e., the structure distorts, by increasing its cell volume, to avoid placing this band at the Fermi energy. The application of pressure, which reduces the cell volume, can be viewed as removing this electronically-driven structural distortion and moving the charge-reservoir band to the Fermi energy.

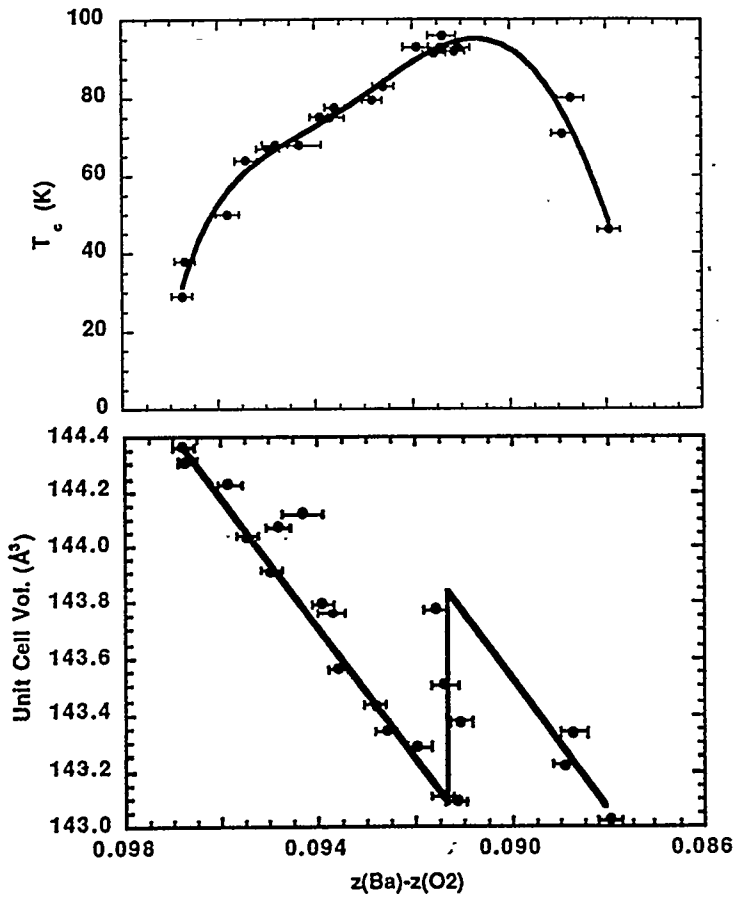

Fig. 2. T_c (top frame) and unit cell volume (bottom frame) of $HgBa_2CuO_{4+x}$ vs. the structural parameter [z(Ba)-z(O2)], which is a measure of the charge transfer (see text).

Such behavior (structural distortion that lowers the density of states at the Fermi energy) is common in conventional superconductors, but has seldom been explicitly studied in the high-T_c materials. However, this behavior is not unique to the $HgBa_2CuO_{4+x}$ compound. A recent study of a chemically-substituted 123 compound in which both the under-doped and over-doped states can be accessed by changing the oxygen content

shows a similar electronically-driven structural distortion at the maximum T_c.[14] In the 123 compound, the structural distortion manifests itself as an increased buckling of the CuO_2 planes, which we have already argued will lower T_c.

The challenge of achieving a higher T_c in the layered copper-oxide compounds is, thus, not an easy task. The desired criteria are well understood, but more than one chemical and/or structural variable is needed to simultaneously achieve the ideal structural and electronic properties. Recent work suggests that, as this ideal compound is approached, electronically-driven structural distortions can suppress T_c by distorting the structure to avoid the ideal structural and/or electronic properties. In spite of these challenges, the T_c of over 160 K achieved in the $HgBa_2Ca_2Cu_3O_{8+x}$ compound at high pressure (in a compound with buckled planes) argues that further increases in T_c at ambient pressure should be possible.

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