NOVEL STRUCTURAL PHENOMENA AT THE MAXIMUM T_C IN 123 AND HgBa2CuO4+ó SUPERCONDUCTORS: EVIDENCE FOR A STRUCTURAL RESPONSE THAT COMPETES WITH SUPERCONDUCTIVITY

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April 1998

This work is supported by the Division of Materials Sciences, Office of Basic Energy Sciences of DOE, under Contract No. W-31-109-ENG-38

DISCLAIMER

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Invited paper for the Proceedings of the NATO Advanced Research Workshop "High-Temperature Superconductors and Novel Inorganic Materials Engineering" held at Moscow State University, March 24-29, 1998. To be published by Kluwer Academic Publishers B.V. in a volume in the NATO book series with the title Chemistry and Technology of High-Temperature Superconductors and Related Advanced Materials, edited by G. VanTendeloo.

Submitted 27 April 1998

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Abstract

Structural distortions that compete with superconductivity have been investigated in two systems where oxygen content can be used to vary the doping continuously from the under doped state, through the maximum T_c into the over doped state. In the 123 system, $(La_{1-x}Ca_x)(Ba_{1.75-x}La_{0.25+x})Cu_3O_{7+\delta}$, the buckling of the CuO_2 planes goes through a maximum at the maximum T_c. In $HgBa_2CuO_{4+\delta}$, where buckling of the CuO_2 planes is not available as a structural degree of freedom, there is a plateau at the maximum T_c where the unit cell volume expands as oxygen is added while the charge transfer and T_c remain constant. These unusual structural phenomena upon crossing through the maximum T_c are hypothesized to be a response of the crystal structure to the electronic structure, with the structural distortions competing with superconductivity, or lowering the T_c from what it would otherwise be.

1. Introduction

Structural distortions that compete with, or destroy, superconductivity are a common feature of conventional superconductors.[1-5] The general argument for explaining such behavior has been that as chemical or structural variables are changed to increase T_c by raising the electronic density of states, the free energy can be lowered by distorting the structure to open a gap at the Fermi energy, transforming the material to an insulator. No analogous behavior has been reported in the high-T_c superconductors: that is, there is no case where a structural distortion or phase transformation destroys superconductivity upon varying the chemistry to increase T_c and, thereby, places a limit on the maximum T_c. However, there is ample evidence for a close connection between T_c and particular features of the crystal structure. In the $La_{2-x}M_xCuO_4$ system, several experiments have demonstrated a relationship between the buckling angle of the CuO_2 planes and T_c.[6-9] When the buckling angle is varied by the application of pressure or chemical substitution, T_c decreases with increasing buckling angle. The observation of an unusual phase separation phenomena at the maximum T_c in $YBa_2Cu_3O_{6+\delta}$, with the two phases having different buckling angles and different T_c's, leads to the same conclusion for that compound.[10] In the present work, we investigate the crystal structure and superconducting properties of two high-T_c systems where the doping can be varied continuously through the maximum T_c. We interpret the behavior of T_c and the crystal structure as both being responses to the changing electronic structure as the doping is varied. In both systems, there is a structural distortion at the maximum T_c that competes with superconductivity, lowering T_c from what it would otherwise be.

2. CuO_2 Plane Buckling in the 123 Structure

$(La_{1-x}Ca_x)(Ba_{1.75-x}La_{0.25+x})Cu_3O_{7+\delta}$ is a compound with the 123 structure in which oxygen content can be used to continuously vary the doping from the under doped regime, through the maximum T_c, far into the over doped regime.[11] Powder samples with x=0.1. and 0.4 were synthesized by the methods described previously [11]. Oxygen contents were varied by subsequent annealing of parts of these initial samples in oxygen pressures from 10^{-4} to 1100 atm. The samples were confirmed to be single phase by x-ray and neutron diffraction. The oxygen contents of the samples were determined by iodometric titration and T_c's were obtained from magnetic susceptibility and resistivity measurements. Sharp superconducting transitions were observed for all samples. Time-of-flight neutron powder diffraction data were collected at room temperature on the Special Environment Powder Diffractometer (SEPD) at Argonne's Intense Pulsed Neutron Source (IPNS) [12] and analyzed by the Rietveld technique using the GSAS code [13] over a d-spacing range of 0.5 to 4 Å, which included up to 597 Bragg peaks.

The structures are tetragonal, space group P4/mmm, at all compositions as a result of the La substitution on the Ba site disrupting the normal oxygen chain ordering. The same defect chemistry -- partial occupancy of the single oxygen site in the "chain-Cu" plane -- is observed in the under doped and over doped regimes. This means that oxygen content can be used to vary the carrier concentration smoothly from the under doped regime to the over doped regime. The metal-site substitutions and the total oxygen contents of the samples determined from the neutron refinements are in agree-

ment with the starting composition and with titration. Oxygen contents as high as 7.3 were achieved in both the x=0.1 and x=0.4 systems. The lattice parameters vary linearly with oxygen content. The Cu2-O4 apical copper-oxygen bond length also varies linearly over the full range, suggesting a smoothly increasing charge transfer. Thus, the hole concentration in the CuO_2 planes, deduced from bond valence sum calculations, increases linearly with oxygen content, as shown in Fig. 1. These results confirm that the hole concentration scales with oxygen concentration over the entire composition range.

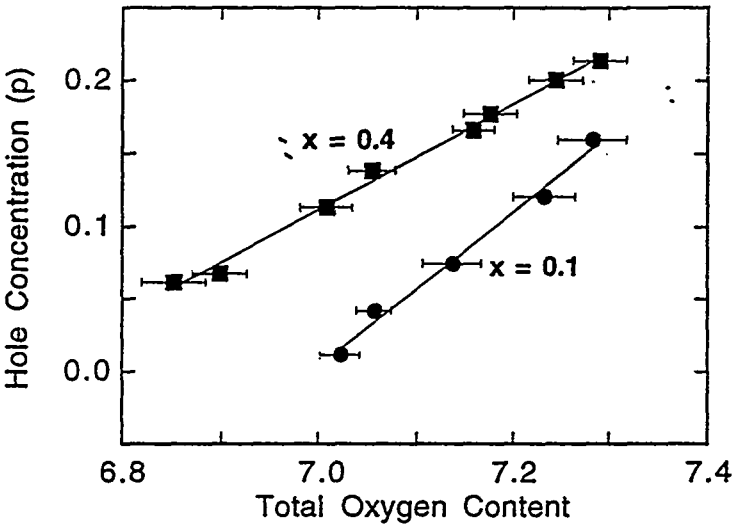

Figure 1. Hole concentration per CuO_2 plane vs. total oxygen for $(La_{1-x}Ca_x)(Ba_{1.75-x}La_{0.25+x})Cu_3O_{7+\delta}$. Round symbols are for x=0.1; square symbols are for x=0.4.

For both the x=0.1 and x=0.4 compounds, a clear maximum in T_c is observed at a total oxygen content of about 7.15, as shown in Fig. 2. The buckling of the CuO_2 planes (defined as the angle by which the plane oxygen atoms are out of the plane of the copper atoms) also goes through a maximum at the same oxygen content, as is shown in Fig. 2. The relationship between T_c and buckling angle is the same in the under doped and over doped regimes, within our experimental uncertainties. This remarkable scaling of the buckling angle and T_c in both the under doped and over doped regimes, while all other structural parameters that are sensitive to charge transfer show only monotonically changing behavior over the whole range, leads us to conclude that the buckling is a response to the same feature of the electronic structure that controls T_c. Thus, we argue that the buckling angle is an indirect probe of the Fermi surface topology.

Drawing on the arguments put forward for conventional superconductors (discussed in the introduction) our results for this 123 system can be understood within the framework of the following assumptions: (1) T_c increases with increasing electronic density of states at the Fermi energy. (2) The free energy of the system increases with increas-

ing electronic density of states at the Fermi energy. (3) If possible, the structure will relax/distort to minimize the free energy. Thus, the maximum relaxation/distortion will occur when the Fermi energy is at a peak in the density of states.

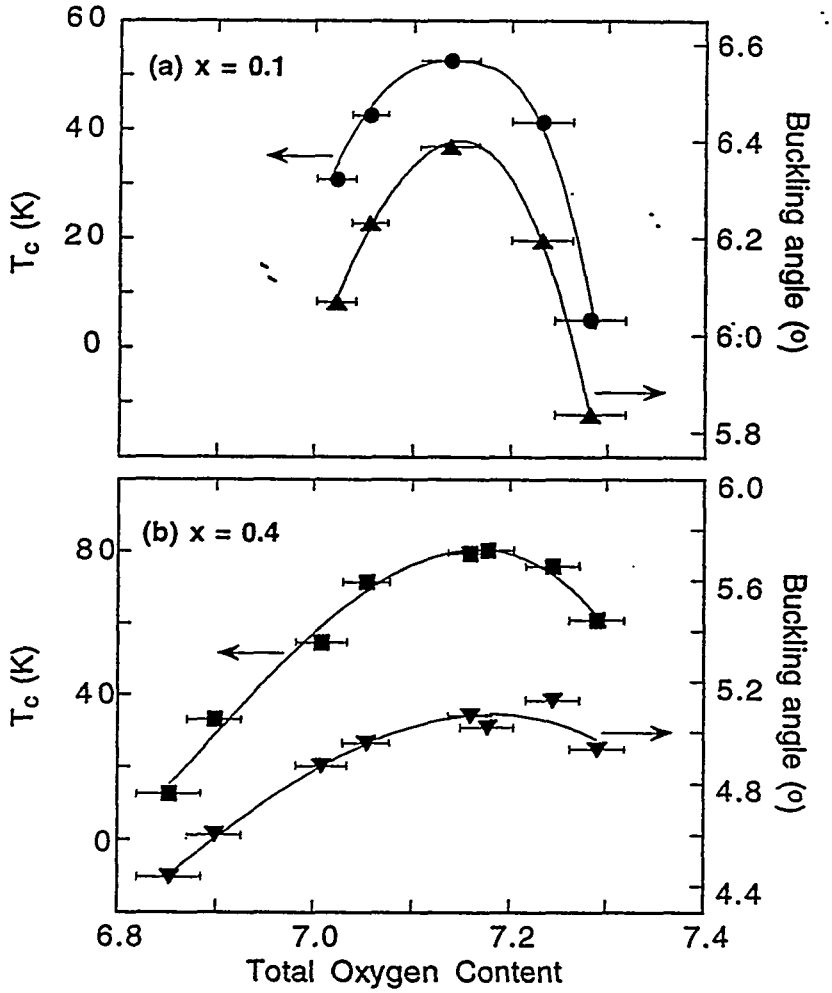

Figure 2. T_c (from resistivity measurements) and buckling angle of the CuO_2 plane vs. total oxygen content for $(La_{1-x}Ca_x)(Ba_{1.75-x}La_{0.25+x})Cu_3O_{7+\delta}$ with x=0.1 (a) and x=0.4 (b).

The buckling of the CuO_2 planes is the structural parameter that is expected to be most sensitive to the relevant features of the electronic structure. Band structure calculations [14] and photoemission studies [15] for the $YBa_2Cu_3O_{6+\delta}$ structure show that the CuO_2 planes and the one-dimensional CuO chains both contribute to the peak in the density of states, but that the chain contribution diminishes as the chain oxygen is depleted and disordered. The 123 compound we have studied is tetragonal and does not

contain ordered CuO chains. At most, it can have only disordered chain fragments in the "chain plane," consistent with the average tetragonal symmetry. Its electronic structure has not been calculated, but we assume that the CuO_2 planes are the dominant contribution to peak in the density of states. Buckling would be expected to modify the Fermi surface so as to lower and/or broaden the peak, as has been calculated [16] and shown experimentally [6-9] for the La_2CuO_4 structure. Thus, the observed changes in buckling angle vs. oxygen content indicate that the structure distorts to lower its free energy as the Fermi energy passes though the peak in the density of states.

3. Cell Volume Expansion in the $HgBa_2CuO_{4+\delta}$ Structure

In light of these results, it is important to ask what structural distortion that competes with superconductivity will occur in a high-T_c compound where CuO_2 plane buckling is not available as a structural degree of freedom. The $HgBa_2CuO_{4+\delta}$ system, where the CuO_2 planes are constrained by symmetry to be flat, [17] offers an opportunity to investigate this question.

A single batch of $HgBa_2CuO_{4+\delta}$ powder was divided into smaller samples which were annealed at 300-400°C in oxygen partial pressures from 10^{-7} to 150 atm to produce samples with oxygen contents over the range $0.01 \leq x \leq 0.22$. T_c's were determined from ac susceptibility measurements and oxygen contents were determined by Rietveld refinement using neutron powder diffraction data.

The T_c's as a function of oxygen content are shown in Fig. 3. The samples clearly extend from the under doped regime, through the maximum T_c, into the over doped regime. The maximum T_c is nominally constant for oxygen contents from $x \approx 0.06$ to 0.16, giving a well defined plateau. The presence of the plateau shows that oxygen content alone is not sufficient to uniquely determine the T_c. It is instructive to

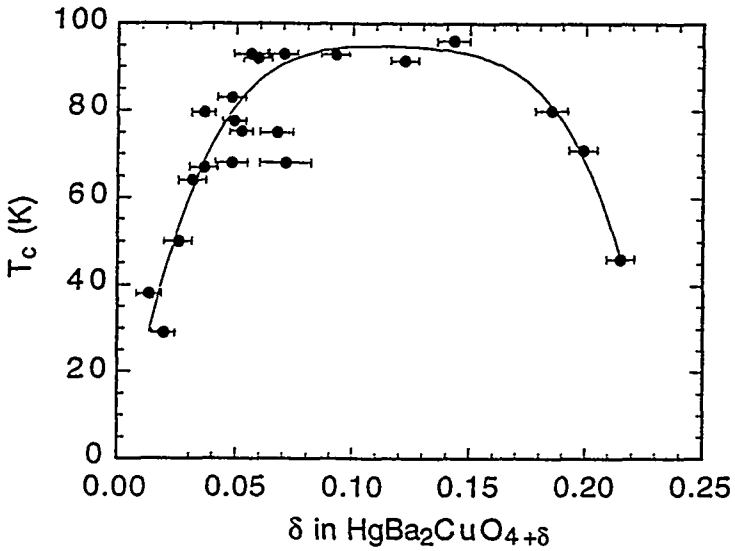

Figure 3. T_c vs. oxygen content for $HgBa_2CuO_{4+\delta}$.

plot T_c as a function of the amount of charge transfer. The structural variables most sensitive to charge transfer are the z coordinates of the Ba and apical O (O2) atoms. These atoms can be viewed as moving up or down (in opposite directions) along the z direction in response to the charges in the CuO_2 plane and the Hg-O_δ layer. Thus, the parameter most sensitive to the charge transfer is [z(Ba)-z(O2)]. Fig. 4a shows T_c plotted as a function of [z(Ba)-z(O2)]. The T_c data map onto a smooth curve when plotted with respect to this variable with the data at maximum T_c clustered around a single point. Thus, these maximum T_c's all correspond to the same charge transfer, in spite of the different oxygen contents.

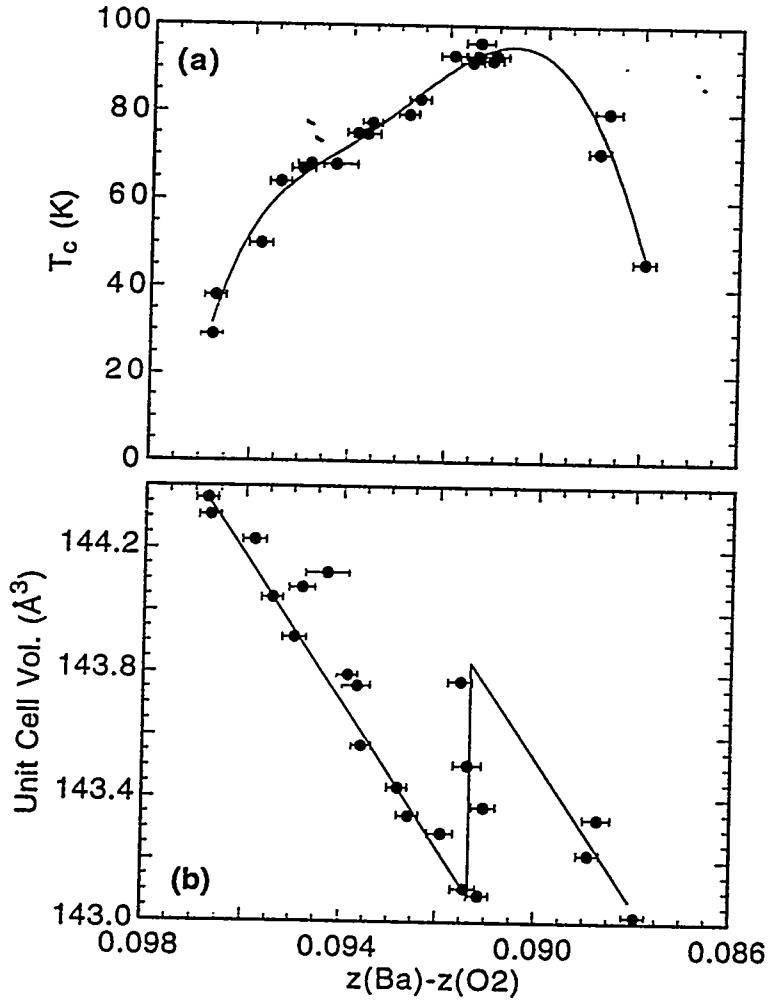

Figure 4. (a) T_c and (b) unit cell volume of $HgBa_2CuO_{4+\delta}$ vs. the structural parameter [z(Ba)-z(O2)], which is a measure of the charge transfer.

As oxygen is added to cross the plateau, the charge transfer remains constant as a result of a structural distortion that occurs over this range of oxygen compositions. This can be clearly seen by plotting structural variables as a function of [z(Ba)-z(O2)]. Fig. 4b shows the behavior of the unit cell volume. In the under doped and over doped regimes, the unit cell volume decreases smoothly with increasing charge transfer, with nominally the same slope. However, in the plateau region, where both charge transfer and T_c are constant, the volume increases. We interpret this unusual increase in cell volume as a response to features of the electronic structure at the maximum T_c. The increasing cell volume results in a constant charge transfer and T_c in spite of the increasing oxygen content. This effect produces the plateau in T_c rather than the expected inverse parabolic behavior.

One important implication of this hypothesis is that the maximum T_c of $HgBa_2CuO_{4+\delta}$ would be considerably higher if the structural distortion could be suppressed. Because the distortion is manifest as an increase in the cell volume, the application of pressure is an obvious way to attempt to suppress the distortion. Ignoring other effects of pressure on T_c, one would predict that pressure would substantially raise T_c for optimally doped samples; but, that the pressure effects would be much smaller for under doped and over doped samples. Qui et al. have reported the pressure dependence of T_c for $HgBa_2CuO_{4+\delta}$ for a range of oxygen contents extending into the over doped regime.[18] Their results are consistent with the prediction. The largest pressure-induced increases in T_c are observed for optimally doped samples. For over doped samples, applied pressure reduces T_c by a small amount.

4. Conclusions

These results show that high-T_c superconductors exhibit structural distortions that compete with superconductivity. Thus, the distortions are largest at the maximum T_c. These distortions are thought to be a response to the same features of the electronic structure that give rise to the high T_c. In the case of the 123 structure, the relevant distortion is buckling of the CuO_2 planes, which is known from other experiments to lower T_c. In the case of the $HgBa_2CuO_{4+\delta}$ structure, the distortion is an unusual expansion of the unit cell volume, which is expected from pressure experiments on this compound to lower T_c. In contrast to the behavior often observed in conventional superconductors, these structural distortions do not give rise to a phase transformation that destroys superconductivity. However, we conclude that the distortion lowers the maximum T_c and that the maximum T_c would be increased if the distortion could be suppressed.

Acknowledgments

This work was funded by the US Department of Energy, Division of Basic Energy Sciences - Materials Science, contract No. W-31-109-ENG-38 (JDJ, DGH, SS, JFM, JPH), the National Science Foundation, Office of Science and Technology Centers, grant No. DMR 91-20000 (OC, HS, BD), and the Israel Science Foundation (AK, YE).

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