



STRUCTURAL BEHAVIOR AND SUPERCONDUCTIVITY OF $\text{YBa}_2\text{Cu}_3\text{O}_x$

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The compound $\text{YBa}_2\text{Cu}_3\text{O}_x$ was given various oxidation treatments over a range of oxygen pressures from 0.02 to 200 MPa and temperatures up to 1223K. A tetragonal to orthorhombic phase transformation was observed, leading to superconducting behavior below 94K. The orthorhombic unit cell parameters (i.e. volume, bond lengths, and axial distortions) were found to correlate with the superconducting transition temperatures. These correlations are rationalized in terms of the interrelationship of oxygen stoichiometry with the lattice parameters of the orthorhombic phase. The nature of superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_x$ and La_2CuO_4 is related to the Cu-O coordination polyhedra and an explanation is proposed for the observed multiple superconducting transitions in $\text{YBa}_2\text{Cu}_3\text{O}_x$.

The superconducting compound $\text{YBa}_2\text{Cu}_3\text{O}_x$ with a transition temperature (T_c) around 92K contains oxygen vacancies in an ABO_3 perovskite structure. Its superconductivity is sensitive to the oxygen content and hence the preparation procedure^{1,2}. A dramatic trend indicating the temperature dependence of resistivity was found in samples quenched in an oxygen atmosphere at different temperatures. As shown in Figure 1, a sharp superconducting transition with T_c at 92K is observed only in slowly cooled samples, whereas those quenched above 800K exhibited semiconducting behavior. Other evidence^{2,3}

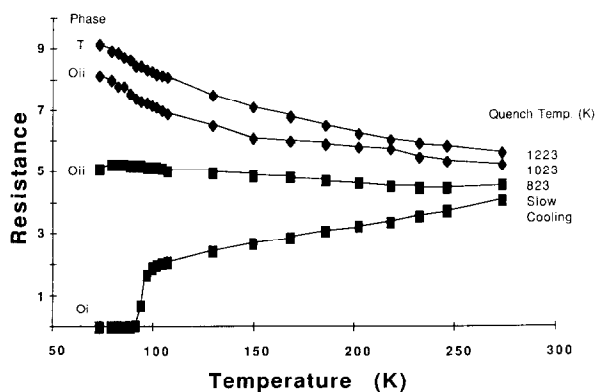


Figure 1. Temperature dependence of resistance for samples quenched from various temperatures.

suggests that the number of oxygen vacancies increases at higher temperatures due to the reduction of Cu ions, and that the best superconductor has $x=7$ oxygens in the above formula. In this report, we present new experimental results which elucidate the structural changes during various

oxidation treatments, including a tetragonal to orthorhombic transition which occurs at different temperatures depending on the oxygen content. We further correlate the superconducting temperature with the orthorhombic lattice parameters and lattice distortion. A structural interpretation based on the electrostatic interactions between oxygen vacancies is provided.

Experiments on oxidation of $\text{YBa}_2\text{Cu}_3\text{O}_x$ covering a range of oxygen pressures from 0.02 to 200 MPa and temperatures up to 1223K were used to effect modifications to the perovskite structure via exchange of oxygen anions and their vacancies. Starting samples were prepared both by mixing BaCO_3 , Y_2O_3 and CuO powders and by co-precipitation of Y-Ba-Cu oxalate from an acidic solution. After calcination, isostatically pressed pellets or plates were sintered at 1223K in flowing oxygen, then slowly cooled. After further oxidation treatment, the crystal structures were analyzed by X-ray diffraction using Cu metal as an internal standard. The resistivities were measured by a four-point probe method with the T_c determined when the resistivity vanished and the ohmic behavior disappeared.

The phases identified at room temperature for samples quenched from various oxygen pressures and temperatures are summarized in Figure 2, with the T_c shown adjacent to the data points. The nomenclature used here is: T for the tetragonal phase ($a=b<c/3$), Oii for the orthorhombic phase when $a<b<c/3$, and Oi for the orthorhombic phase when $a<b=c/3$. The c axis is taken to be the direction along which the cations Ba-Y-Ba are stacked. Two prominent series of X-ray diffraction peaks illustrating the above three cases are schematically shown in Figure 3. Previously, Gallagher et al.³ attributed the Oii regime to the coexistence of Oi and T. However, both our data and theirs indicate that the orthorhombic lattice continuously distorts from Oii to Oi, due to the temperature and (oxygen) composition dependence of b and c . Thus, only one transformation, from tetragonal to orthorhombic, occurs as the oxygen content of the perovskite structure increases, and there is no evidence for a two phase region. The orthorhombic lattice near the phase boundary is characterized by $a<b<c/3$ giving the appearance of Oii reflections in Figure 3, a single phase isomorphic with Oi.

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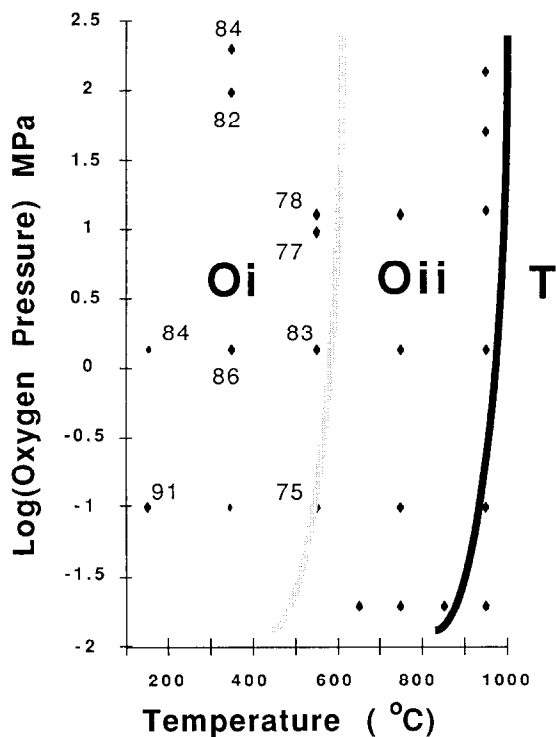


Figure 2. Phase identified at room temperature after oxygen treatment at various conditions.

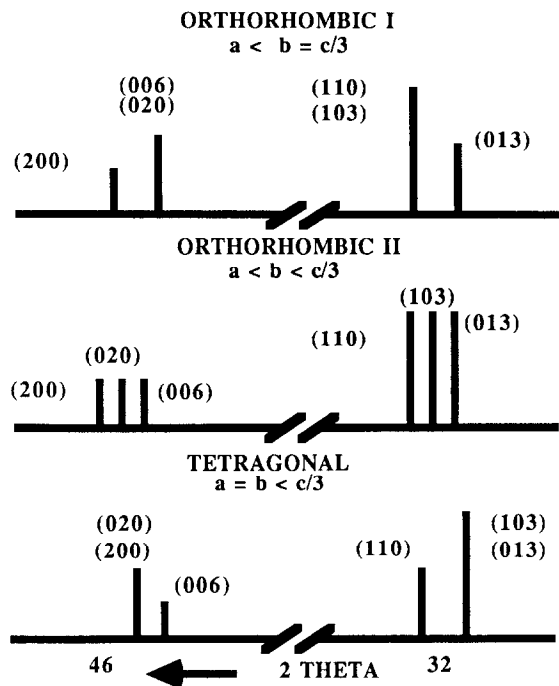


Figure 3. Schematics of {200} and {013} reflections (using $\text{CuK}\alpha$ X-ray) for the tetragonal to orthorhombic phase transformation.

The above transformation is believed to be a ferro-elastic distortion which is common among perovskites. A similar transformation was also reported recently for the high T_c (40K) superconductor $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ at 180K⁴. This transformation should be second order, reversible, and free from hysteresis in the absence of a nucleation barrier. In the present compound, the transformation temperature is lowered as the oxygen content is reduced. The tetragonal phase is stable at room temperature when the oxygen content is lower than 6.45³.

Low temperature x-ray diffraction indicates that the Oi phase remains stable to at least 20K, well beyond the superconducting transition temperature. Continuing studies are underway to examine the effect of oxygen on the orthorhombic to tetragonal transformation and the variation of the cell parameters of the tetragonal phase.

As apparent from Figure 2, it is the Oi polytype which manifests high T_c superconductivity. We have investigated the possible correlations between the orthorhombic lattice parameters and superconductivity. These results are summarized in Figures 4-6, in which the shortest lattice parameter a , the largest orthorhombic axial distortion $c/3-a$, and the unit cell volume are plotted against T_c . (In these plots, the highest T_c samples from this study and similar ones from several recent studies^{3,5,6} are highlighted as open circles.) Despite the considerable scattering which we will address later, correlations between the above quantities appear plausible. Referring to the structure (Figure 7) determined by high resolution neutron diffraction^{6,7}, we can readily interpret the above results to suggest that a short Cu1-Oxygen vacancy-Cu1 distance, a large Jahn-Teller distortion, and a compact cell generally favor high T_c superconductivity.

We now briefly comment on the possible sources of data scattering in the above correlations. First, given that a unique structural correlation of the functional form T_c versus a , b , or c indeed exists, plotting T_c against any one of the three lattice parameters, or some form of their combinations, as we did in Figures 4-6, generally will not give a close correlation. This may be related to simultaneous modification of the other two lattice parameters, thus obscuring one dimensional correlations. Second, our T_c data represent the null resistivity temperatures at which ohmic behavior disappeared. In some samples, while initial

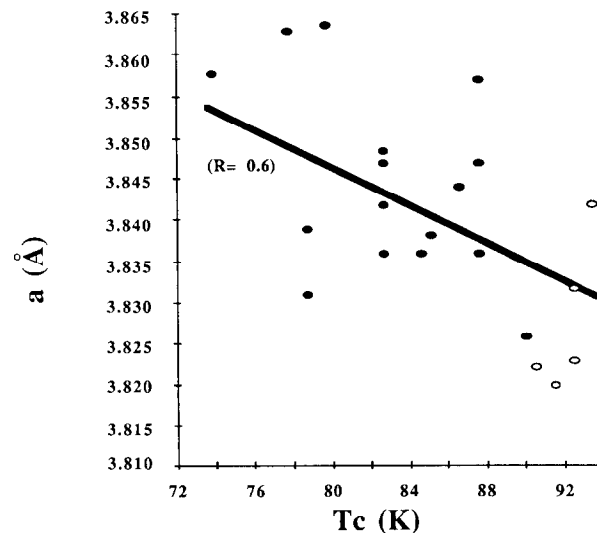


Figure 4. T_c dependence of the shortest lattice parameter, i.e. the Cu1-Cu1 spacing.

Table 1
Interatomic distances (Å) for $\text{YBa}_2\text{Cu}_3\text{O}_7$

Bond	Calculated†	Observed††	Difference
Y - O2	2.369	2.415	+0.046
Y - O3	2.369	2.378	+0.009
Ba - O1	2.820	2.879	+0.059
Ba - O2	2.820	2.976	+0.156
Ba - O3	2.820	2.970	+0.150
Ba - O4	2.820	2.743	-0.077
Cu1 - O1	1.890	1.943	+0.053
Cu1 - O4	1.890	1.850	-0.040
Cu2 - O2	2.000	1.928	-0.072
Cu2 - O3	2.000	1.962	-0.038
Cu2 - O4	2.000	2.303	+0.303

† Calculated from Table of Effective Ionic Radii in Ref. 7. $r_Y(1.019)$,
 $r_{Ba}(1.52)$, $r_{Cu1}(0.54)$, $r_{Cu2}(0.65)$, $r_{O1}(1.35)$, $r_{O2}(1.35)$, $r_{O3}(1.35)$,
 $r_{O4}(1.35)$, all radii in Å.

†† Distances determined via neutron scattering reported in Ref. 3.

decreases in magnetic susceptibility at temperatures of 70 and 94K. A comparison of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ structure with that of $\text{La}_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$ provides some interesting clues to the structural origins of superconductivity. Recent neutron powder diffraction data¹³ for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ have shown that the CuO_6 octahedron is elongated parallel to *c*, with four oxygens at 1.889Å and two at 2.411Å coordinating the Cu^{2+} . These octahedra, in turn, are linked to form continuous sheets parallel to {001}.

This structural feature, which leads to superconductivity at 40K in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, is similar to the sheets of Cu^{2+} -O pyramids in $\text{YBa}_2\text{Cu}_3\text{O}_x$ (corresponding to Cu2 in Figure 7). Comparison of the Cu2-O(2,3) and Cu2-O4 bond lengths (Table 1) with those given above shows a nearly identical correspondence despite the change from five- to six-fold coordination. This comparison leads us to speculate that the Cu2-O(2,3) sheets are responsible for the lower temperature (70K) transition in $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ ^{3,13} similar to that occurring in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ at 40K. Continuing with this reasoning, we suggest that the square planar Cu^{3+} -O chains parallel to *b* (Cu1-O1 in Figure 7) in $\text{YBa}_2\text{Cu}_3\text{O}_x$ are the next most similar feature to the Cu-O planes of La_2CuO_4 , and that

superconductivity at 94K in $\text{YBa}_2\text{Cu}_3\text{O}_x$ is associated with Cu1-O1 chains. This hypothesis is consistent with the observed degradation of superconductivity by reducing the oxygen content to less than seven per unit cell, requiring removal of oxygen from the O1 positions, thus disrupting the Cu1-O1 superconducting pathway. The observed resistivity/susceptibility transition gradually decreases from 94 to 70K as connectivity of the Cu1-O1 chains decreases and as the Cu2-O(2,3) superconducting transition temperature is approached.

In conclusion, we have studied the tetragonal to orthorhombic transition and the structure/*T_c* relation in $\text{YBa}_2\text{Cu}_3\text{O}_x$ under various oxidation treatments. Only the orthorhombic phase is superconducting at higher temperatures. Samples with the smallest cell volume, closest Cu-O vacancy-Cu spacing, and the largest axial distortion, have the highest *T_c*. We suggest that this "tuning" of lattice parameters, via Coulombic and rigid ionic sphere interactions, and possibly the accompanying correlations with high temperature directional superconductivity, can be adjusted by controlling compositional parameters such as oxygen/vacancy content.

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