STRUCTURAL PHASE TRANSITION IN $YBa_2Cu_3O_{7-\delta}$:
THE ROLE OF DIMENSIONALITY FOR HIGH TEMPERATURE SUPERCONDUCTIVITY

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We have performed detailed high temperature X-ray diffraction to study
the nature of the structural phase of $YBa_2Cu_3O_{7-\delta}$. The results indicate
the existence of a reversible orthorhombic to tetragonal phase transition
at a temperature close to 750°C. If the high temperature tetragonal
phase is quenched-in at low temperatures the critical superconducting
temperature is considerably reduced from 92.5 K. This suggests that the
one dimensional Cu-O chains present in the orthorhombic structure are
necessary for high temperature superconductivity.

The relationship between the structure and
high temperature superconductivity in the Y-Ba-
Cu-O system is an issue which relates strongly
to the origin of the superconducting mechanism
in the recently discovered high temperature
superconductors.[1-2] It is by now established
that the superconductivity in this system origi-
nates from a compound with a (1:2:3) Y:Ba:Cu
stoichiometry.[3-5] A single crystal diffraction
study by Hazen et al.[6] and Le Page et al.[7] found
a tetragonal structure based on a stacking of 3
perovskite unit cells. However, X-ray powder
diffraction investigations indicate an
orthorhombically distorted variant of this
tetragonal cell.[5,8] None of the above X-ray
studies could conclusively determine the posi-
tions or occupation of the oxygen atoms. Recent
powder neutron diffraction investigations[9,10]
have determined the structure to be orthorhombic
Pmmm. The structure consists of three distorted
perovskite building blocks, which contain Cu
atoms at the corners, O atoms on the cube edges
between the Cu atoms and ordered metal ions (Ba
and Y) in the center of the cube. The Y plane
is totally devoid of oxygen, the Cu-O planes
adjacent to the Y-planes are dimpled with the O
atoms pulled towards the Y, whereas the Cu-O
plane located between Ba-O planes exhibits
ordered O vacancies which results in one
dimensional Cu-O chains along the b-axis. Our
studies, and the conflicting structural reports
in the literature, lead us to believe that there
might be a high-temperature structural phase
transition in this compound.

In this paper we present high temperature
X-ray diffraction data showing an orthorhombic
to tetragonal transition as the stoichiometric
compound is heated above 750°C. If the
tetragonal phase is stabilized at low tempera-
tures by a fast quench, the sample exhibits
superconductivity at a much lower temperature
than the pure orthorhombic phase. This suggests
that the one dimensional Cu-O chains present in
the orthorhombic structure may be responsible
for the superconductivity. If this hypothesis
is correct it has important implications for the
type of mechanisms which are responsible for
superconductivity in high temperature oxides.

Stoichiometric samples with a (1:2:3)
Y:Ba:Cu composition ratio were prepared using
standard powder metallurgical techniques. After
thorough mixing and grinding of Y_2O_3(99.999%),
CuO(99.99%) and $BaCO_3$(99.99%) powders the

samples were sintered in a pure, flowing oxygen atmosphere for 10 hours at 975°C and furnace cooled. We have shown earlier that this preparation method yields an ~95% single-phase compound, which has a superconducting transition temperature of 92.5 K (transition width of 1.5 K) and an orthorhombic structure. The details of the phase diagram and the orthorhombic structure have been the subject of earlier papers.[3,9] X-ray diffraction measurements up to 1000°C have been taken with a Rigaku DMaxII diffractometer in 1 atmosphere of flowing O_2 using 2 KW of CuK_α radiation. The lattice spacings were determined using Cohen's least squares fitting procedure,[11] which removes possible systematic errors introduced by the thermal expansion coefficients of the sample holder and furnace assembly.

Part of the X-ray diffraction patterns as a function of temperature are shown in Figure 1. The 750°C pattern can be indexed with a tetragonal cell with intensities which cor-
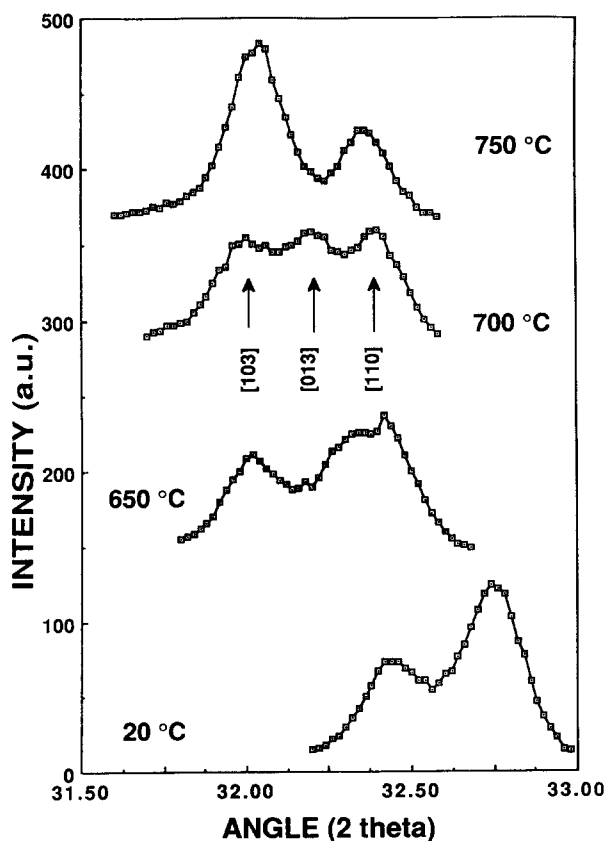
respond well to the structure found by Hazen et al.[6] In both the orthorhombic and tetragonal diffraction patterns the most intense lines consist of doublets but with reversed 2:1 intensity ratios. In the case of the orthorhombic structure at 20°C, the most intense peak of each doublet is an accidental degeneracy (e.g. [103] and [110]), while in the tetragonal phase a true degeneracy leads to the intensity reversal. This is shown very clearly in Fig. 1 where a series of diffraction patterns for the (103), (013), and (110) lines are displayed for various temperatures. As the temperature is increased, from 20°C, the accidental degeneracy of the orthorhombic phase is reversed. The (103) and (013) diffraction peaks merge at the crystallographic phase change.

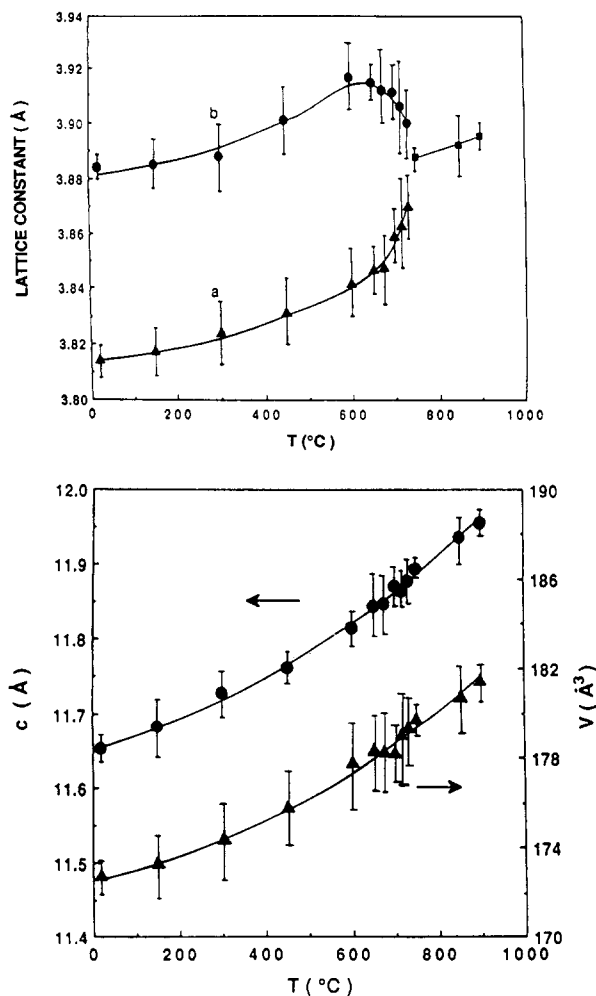Figure 2 shows the temperature dependence

Fig. 1. Selected region of in-situ, temperature dependent, X-ray diffraction intensity for a sample heated in oxygen environment.

Fig. 2. (top): a- and b-lattice constants as a function of temperature. The data is the average of two runs on two different samples.
(bottom): unit cell volume and c-lattice constant as a function of temperature. Note the absence of anomalies through the phase transition.

of the lattice constants and of the unit cell
volume. At around 700°C the lengths of the a
and b axes converge and the structure becomes
tetragonal by 750°C (Fig. 2a) At the transition
the tetragonal a-axis is the average of the
orthorhombic a- and b-axes. The c-axis and the
volume on the other hand show no major features
around this temperature (Fig. 2b). From this it
appears that at the transition there is no large
change in the oxygen concentration. Figure 2
only shows the heating data. On cooling, the
diffraction peaks broaden considerably when
passing through the phase transition. This may
be due to the small grain size of the
orthorhombic phase as it transforms from the
tetragonal structure or a mixed orthorhombic-
tetragonal phase region. In this temperature
region, the diffraction patterns do not change
with time which indicates a mixed phase region.
Well below the phase transition temperature
(~600°C) the diffraction peaks narrow again.
The observed hysteretic behavior of the
transformation indicates the possibility of a
first order phase transition.

In order to study the relationship between
structure and superconductivity we quenched
several samples from 975°C to room temperature,
thus partially stabilizing the high temperature
tetragonal structure. This was confirmed by
detailed X-ray diffraction measurements. The
resistivity of all the samples was measured
before and after quenching, and they all exhibit
similar features. The temperature dependence of
the resistivity of one of the samples is shown
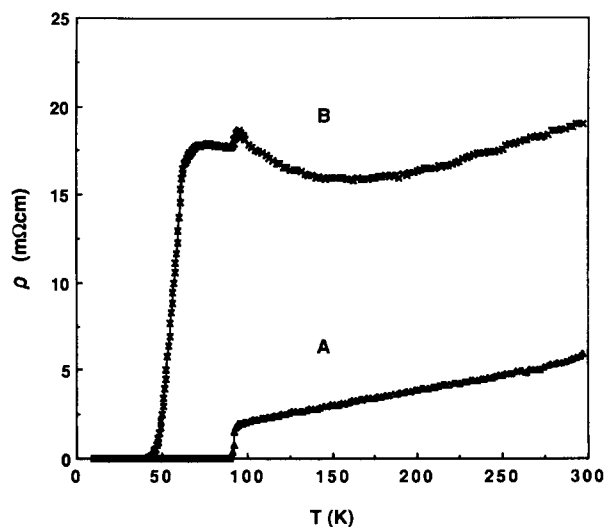in Figure 3. Before quenching, the sample is

Fig. 3. Resistivity of a furnace cooled sample
(A) and the same sample quenched (B).

metallic with a sharp superconducting transition
temperature at 92.5 K (~2 K transition width).

After the quench, the resistivity is much higher
and metallic at high temperature, exhibits a
shallow minimum around 150 K, a small drop at
approximately 92 K (T_c of the single phase
orthorhombic structure) and a superconducting
drop at around 50 K. Although the majority
phase in this sample is tetragonal, it is not
possible to state that the tetragonal phase has
a 50 K superconducting transition. The 50 K
transition could be due to the remaining
orthorhombic material (highly disordered due to
O vacancies etc.) with a lower T_c. However we
can state unambiguously that the tetragonal
structure has a lower transition temperature
than the ordered orthorhombic phase,[9] it may
even be nonsuperconducting.

The present work together with, single
crystal X-ray diffraction[6,7] and preliminary
neutron scattering[12] results for the tetragonal
structure (i.e., only 2-D Cu-O sheets), have
important implications for the possible super-
conducting mechanisms present in this class of
materials. The lattice parameters of the
orthorhombic and tetragonal phases are very
close, so these slight changes (~0.05 Å) cannot
significantly change the wave function overlaps.
The main difference is that in the tetragonal
phase the ordering of the oxygen vacancies in
the Cu-O planes at z = 0 is nonexistent[6,7] and
therefore the one dimensional Cu-O chains are
absent. As the sample is quenched to low
temperature the oxygens remain randomly
distributed and therefore the absence of one
dimensional chains is quenched into the sample.
This together with the fact that this sample
exhibits absence of superconductivity at 92 K
implies that the one dimensional Cu-O chains
play a major role in the mechanism responsible
for the high T_c in this compound. If the one
dimensional chains are responsible for the
superconductivity, the T_c of the quenched sample
might depend very delicately on oxygen vacancies
and details of the preparation method. The lack
of sensitivity of the superconducting transition
temperature to magnetic rare-earth substitutions
(for instance Ho, Gd)[13-16] in the Y site,
supports the contention that the two-dimensional
Cu-O planes are not solely responsible for the
superconductivity. Moreover, if the chains are
responsible for the superconductivity, the Cu-O
planes would screen the effect of the magnetic
ions. A recent discussion[17] of the formal
oxidation states of the two Cu atoms in this
material also concludes that the Cu-O chains are
responsible for the high temperature supercon-
ductivity. This should be compared with the
situation occurring in the La(Ba,Sr)Cu system in
which only two dimensional Cu-O planes are
present and the T_c of the material is in the
35 K region.

In summary, we have performed extensive
structural studies of the orthorhombic to
tetragonal phase transition in the YBaCu system.
The results show a well defined transition at

750°C which does not involve a significant volume change. Quenching experiments together with depression of superconductivity in the tetragonal phase suggests that the superconductivity in the orthorhombic phase requires the existence of the one dimensional Cu-O chains, unlike the La(Ba,Sr)Cu system where only two dimensional Cu-O planes are present.

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