XANES and EXAFS Study of Au-Substituted YBa$_2$Cu$_3$O$_{7-\delta}$

Mark W. Ruckman
Brookhaven National Laboratory
Upton, New York

and

Aloysius F. Hepp
Lewis Research Center
Cleveland, Ohio

Prepared for the
Fourth Annual Conference on Superconductivity and Applications
sponsored by The New York State Institute on Superconductivity
Buffalo, New York, September 18–20, 1990
XANES AND EXAFS STUDY OF Au-SUBSTITUTED YBa2Cu3O7-δ

Mark W. Ruckman
Brookhaven National Laboratory, Upton, NY 11973-5000

Aloysius F. Hepp
NASA Lewis Research Center, Cleveland, OH 44135

ABSTRACT

The near-edge structure (XANES) of the Au L3 and Cu K edges of YBa2Au0.3Cu2.7O7-δ has been studied. X-ray diffraction suggests that Au goes on the Cu(1) site and XANES shows that this has little effect on the oxidation state of the remaining copper. The gold L3 edge develops a white line feature whose position lies between that of trivalent gold oxide (Au2O3) and monovalent potassium gold cyanide (KAu(CN)2) and whose intensity relative to the edge step is smaller than in the two reference compounds. The L3 EXAFS for Au in the superconductor resembles that of Au2O3. However, differences in the envelope of the Fourier filtered component for the first shell suggest that the local structure of the Au in the superconductor is not equivalent to Au2O3.

INTRODUCTION

Substitution of many metals in YBa2Cu3O7-δ (abbreviated as 123 in the following)1-5 usually depresses the transition temperature Tc and has other negative effects on the superconducting properties. Trivalent metal ions like Fe, Co, or Al replace linear chain site copper, the Cu(1) site, and depress Tc more slowly than Zn and Ni which replaces copper located on the CuO22- sheets, the Cu(2) site. XANES studies6-8 indicate that transition metal substitutions on the Cu(1) site usually effect the oxidation state of the Cu(2) site and its associated oxygen, but substitution of zinc has little effect on the oxidation state.9

Noble metals like gold and silver are exceptional in that considerable amounts of Ag can be put into 123 before Tc begins to decrease10, Au/123 junctions have a small contact resistance11,12 and show little evidence of solid state reaction13. This is of obvious practical benefit in the fabrication of any device requiring a junction with a normal metal. Streitz et al.14 examined the microstructure of Au/123 composites and found that separate Au and 123 phases exist after heat treatment in oxygen. They also determined that a small amount of Au (x < 3 atomic %) went into the orthorhombic 123 phase.14 Hepp et al. came to a similar conclusion for YBa2(AuxCu1-x)3O7-δ.15

We report results of an examination of the Cu K and Au L3 edges for YBa2(AuxCu1-x)3O7-δ. Gold substitution of 8 mole % has little effect on the oxidation state of Cu in 123. The appearance of the L3 edge suggests that the oxidation state of Au is lower in the superconductor than Au2O3, and that Au has fewer unoccupied d-states in 123 than in the trivalent oxide. The appearance of the extended x-ray absorption fine structure (EXAFS) of the Au L3 edge supports earlier findings that Au is incorporated in the lattice at this concentration.
EXPERIMENTAL

The samples used in this investigation were synthesized and characterized as previously discussed.\textsuperscript{15} For YBa\(_2\)(Au\(_x\)Cu\(_{1-x}\))O\(_{7-\delta}\), x-ray diffraction (XRD) and x-ray photoemission (XPS) data suggest that trivalent Au goes into the Cu(1) site. When this occurs, the a and b axes remain unchanged but the c axis expands from 11.69 to 11.75 Å. This is in accord with the well known structural chemistry of Au (i.e., Au(III) forms square planar complexes).\textsuperscript{15}

No evidence was found for the formation of secondary phases in the XRD patterns for Au substitutions less than 10 mole \(\%\); formation of a second phase was readily detected in the XRD data when more than 10 mole \(\%\) was put in 123. \(T_c\) was observed to be 89 K for an 8 mole \(\%\) gold containing material and 91 K for the parent 123 material made without Au\(_2O_3\). Very similar conclusions were drawn in a recent study by Cieplak et al.\textsuperscript{16}, but they were unable to produce single-phase material when substituting Au for Cu. We were only able to obtain single-phase material, as determined by XRD and microscopy when using BaO\(_2\) in the synthesis of the material.\textsuperscript{15}

X-ray absorption measurements were made in the transmission mode using powdered samples dispersed on adhesive tape. Au or Cu foil absorbers were placed after the samples to run in conjunction with the samples to maintain a calibrated energy scale. The work was done at the X-IIA beamline at the Brookhaven National Synchrotron Light Source.\textsuperscript{17} The monochromator resolution is estimated to be 1.0 eV at the Cu K-edge and 1.2 eV at the Au L\(_3\) edge. Samples were crushed into powder, screened through 400 mesh and dispersed onto adhesive tape.

The near-edge and EXAFS data for the Cu K and Au L\(_3\) edges was analyzed using standard procedures.\textsuperscript{18} A linear background was removed from the edge before normalization. To extract the EXAFS, the atomic absorption background was approximated by a spline curve. The \(\chi(k)\) data was converted from energy space to \(k\)-space assuming an \(E_0\) for Cu of 8992 eV and 11,919 eV for Au. The Fourier transforms were computed using a Gaussian window function to obtain a quantity related to the radial distribution function around the absorbing atom.

RESULTS AND DISCUSSION

The Cu K edges for the 123 material (solid line) and the 8 mole percent Au sample (dashed line) are shown in Fig. 1. The Cu K edge is complex and several interpretations of it exist.\textsuperscript{19-23} XANES results are now available for highly oriented powders or single crystal materials using polarized x-rays and these provide more reliable data on the Cu K edge.\textsuperscript{24-27} The Cu K near-edge structure arises from dipole transitions from the Cu 1s core level to the low-lying copper valence or conduction band states with \(p\) or \(\pi\) symmetry and to transitions from the Cu 1s to continuum final states that are modified by multiple scattering (shape resonances). The transitions to bound final states are related to the electron density of states and are sensitive to changes in the chemical state of the Cu while the shape resonances are sensitive to structural modification. Heald et al.\textsuperscript{24} examined the Cu K edge from 123 powders oriented such that the x-ray polarization
accompanied by shake down transitions \((4p_\sigma^*)\) and peak "C" contains contributions from the \(4s\) to \(4p_F\) and \(4s\) to \(4p_0\) transitions from the Cu(2) and the Cu(1) sites. The feature marked "D" is identified as a shape resonance. Figure 1 shows the Cu K edges of YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) and YBa\(_2\)Au\(_{0.3}\)Cu\(_{2.7}\)O\(_{7-\delta}\) to be virtually identical. This suggests that Au substitution has little or no effect on the valence of copper on either site and that the Cu is still formally divalent.

The Au L\(_3\) edges for YBa\(_2\)(Au\(_{x}\)Cu\(_{1-x}\))\(_3\)O\(_{7-\delta}\), Au foil, monovalent KAu(CN)\(_2\), and trivalent Au\(_2\)O\(_3\) are shown in figure 2. The spectra for the reference compounds and Au substituted 123 have been normalized to the edge step of the Au absorption edge. The near-edge structure of the L\(_2\) and L\(_3\) edges in 5d transition metal compounds is dominated by 2p\(_{1/2}\) to 5d\(_{3/2}\) and 2p\(_{3/2}\) to 5d\(_{3/2}\) transitions (white line feature).\(^{30,31}\) The L\(_3\) edge also has a contribution from the 2p\(_{3/2}\) to 5d\(_{3/2}\) but it is much weaker than the 2p\(_{1/2}\) to 5d\(_{3/2}\) and \(\vec{e}\) was either parallel or perpendicular to the \(c\) axis. The position of a weak pre-edge feature marked "A" due to \(ls\) to 3d quadrupole transitions is marked on figure 1 and it is directly related to the valence of the Cu. In oxygen deficient 123 material, this peak grows in proportion to the removal of holes from the Cu site and the formation of Cu.\(^{28,29}\) Peak "B" is due to transitions from the \(ls\) to \(4p_\sigma\) band (Cu(l) and Cu(2) sites) accompanied by shake down transitions \((4p_\pi^*)\) and peak "C" contains contributions from the \(ls\) to \(4p_\sigma\) and \(ls\) to \(4p_\sigma\) transitions from the Cu(2) and the Cu(l) sites. The feature marked "D" is identified as a shape resonance. Figure 1 shows the Cu K edges of YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) and YBa\(_2\)(Au\(_{x}\)Cu\(_{1-x}\))\(_3\)O\(_{7-\delta}\) to be virtually identical. This suggests that Au substitution has little or no effect on the valence of copper on either site and that the Cu is still formally divalent.

The Au L\(_3\) edges for YBa\(_2\)(Au\(_{x}\)Cu\(_{1-x}\))\(_3\)O\(_{7-\delta}\), Au foil, monovalent KAu(CN)\(_2\), and trivalent Au\(_2\)O\(_3\) are shown in figure 2. The spectra for the reference compounds and Au substituted 123 have been normalized to the edge step of the Au absorption edge. The near-edge structure of the L\(_2\) and L\(_3\) edges in 5d transition metal compounds is dominated by 2p\(_{1/2}\) to 5d\(_{3/2}\) and 2p\(_{3/2}\) to 5d\(_{3/2}\) transitions (white line feature).\(^{30,31}\) The L\(_3\) edge also has a contribution from the 2p\(_{3/2}\) to 5d\(_{3/2}\) but it is much weaker than the 2p\(_{1/2}\) to 5d\(_{3/2}\) and
2p_{3/2} to 5d_{5/2} transitions. The intensity of this feature is thought
to provide a good probe of the 5d-band occupation.\textsuperscript{32} For Au (small
dashed curve), the 5d band is filled and no white line feature is
observed at the L\textsubscript{2} edge. The oxidation of Au to the mono- or trivalent
state creates the white line feature. We find that the white line area
is a little larger for Au\textsubscript{2}O\textsubscript{3} (dot-dashed line) than KAu(CN)\textsubscript{2} (dashed
line) and also find that the white line feature shifts to lower photon
energy when the oxidation number increases from +1 to +3. It should
be noted that the ratio of the white line areas for Au\textsubscript{2}O\textsubscript{3} and KAu(CN)\textsubscript{2}
is less than the ratio of d-electron removal suggested by the valence.
This means that the actual d-band occupation changes less than expected
from simple electron counting. The white line area for Au in 123 (solid
line) is smaller than either of the reference compounds and the white
line lies at lower energy than KAu(CN)\textsubscript{2}.

From Au L\textsubscript{2} near-edge data presented for YBa\textsubscript{2}(Au\textsubscript{0.1}Cu\textsubscript{0.9})\textsubscript{3}O\textsubscript{7-δ}, it
is clear that the electronic structure of Au in 123 differs from that
of Au in trivalent Au\textsubscript{2}O\textsubscript{3}. Hepp et al.\textsuperscript{15} made an assignment of the
trivalent state for Au in the 123 material using XPS measurements of
the Au 4f\textsubscript{1/2} core level. We believe the L\textsubscript{2} near-edge data shows that
oxidation state of Au in the 123 material is not equivalent to that of
Au in the formally trivalent oxide. Au may be "formally" trivalent in
this material but significant departures in the 5d band occupation seem
to be taking place. Trivalent Fe also replaces Cu on the chain site.
However, substitution of the same amount of Fe depresses T\textsubscript{c} by 55 K\textsuperscript{33}
rather than the 2 K found for Au. Yang et al.\textsuperscript{6} found that the Fe
substitution modifies the O K edge and reduces the number of 2p holes
on the oxygen. We speculate that the reduction in the apparent number
of unoccupied Au 5d states for Au in 123 when compared to Au in Au\textsubscript{2}O\textsubscript{3}
and the small Au induced change in T\textsubscript{c} implies that little or no change
occurs in the number of the oxygen 2p holes. This is supported by
our data for the Cu K edge which shows no change in the Cu-O bonding
like that observed when the high T\textsubscript{c} material becomes oxygen deficient
and holes are removed from the copper and oxygen.\textsuperscript{26} We also speculate
that the placement of holes on the oxygen nearest neighbors reduces the
hybridization of Au 5d states\textsuperscript{32} and this is responsible for the smaller
L\textsubscript{3} white line area for Au in 123 when compared to Au(III) oxide.

The χ(k) data extracted from the L\textsubscript{3} edge is shown in figure 3 for
YBa\textsubscript{2}(Au\textsubscript{0.1}Cu\textsubscript{0.9})\textsubscript{3}O\textsubscript{7-δ} (a), Au\textsubscript{2}O\textsubscript{3} (b), and Au (c). The data are k\textsuperscript{2}
-weighted to enhance the amplitude of high-k oscillations. The Au L\textsubscript{3}
EXAFS functions for Au substituted 123 and Au\textsubscript{2}O\textsubscript{3} look similar and are
very different from that obtained for Au. The reduction in the
strength of the EXAFS oscillations as a function of k suggests that the
Au in the superconductor is coordinated by light elements like oxygen
rather than a heavy element like Au.\textsuperscript{33}

The appearance of the Au L\textsubscript{3} EXAFS provides support for our
interpretation of the Au L\textsubscript{3} edge discussed earlier. The reduced
strength of the white line could be rationalized by assuming that the
L\textsubscript{3} edge is the sum of an oxidized Au component and metallic Au.
However, a significant fraction of the Au would have to be in the
metallic phase to account for the XANES result. If the Au particles are
so small as to preclude getting EXAFS from the Au, it is difficult to
see how the gold could have the metallic electronic structure.\textsuperscript{34} Hence,
we conclude that the gold has not formed a separate metallic component as seen during the formation of 123/Au composites.

In figure 4, the Fourier transforms of the $k^2$-weighted $L_3 \chi(k)$ data for $\text{YBa}_2(\text{Au}_{0.1}\text{Cu}_{0.9})_3\text{O}_{7-\delta}$ (solid line) and $\text{Au}_2\text{O}_3$ (dashed line) are shown. The Fourier transformed EXAFS for both $\text{YBa}_2(\text{Au}_{0.1}\text{Cu}_{0.9})_3\text{O}_{7-\delta}$ and $\text{Au}_2\text{O}_3$ shows a peak located at a radial coordinate of 1.6 Å. This value is close to the first shell radial coordinate measured for copper by a number of groups\textsuperscript{35-37} and ourselves for 123 (not shown); detailed analysis of the copper EXAFS\textsuperscript{35} indicates a Cu-O spacing of 1.9 Å for the Cu(1)-O bond. Hepp et al.\textsuperscript{15} found Au substitution causes little change in the $a$ and $b$ lattice constants and we think the Au-O spacing is nearly equal to that of Cu-O. Detailed analysis of the Au $L_3$ EXAFS data is hampered by the lack of a suitable Au-O standard.\textsuperscript{38} To the best of our knowledge, a detailed structural study of $\text{Au}_2\text{O}_3$ has not been performed. We think that $\text{Au}_2\text{O}_3$ is highly disordered because the Fourier transformed EXAFS for $\text{Au}_2\text{O}_3$ shows only the single peak corresponding to the first shell. Figure 4 shows a second peak at 2.7 Å for the Au-substituted 123 material. X-ray\textsuperscript{39} and neutron scattering\textsuperscript{40} studies of the structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ indicate that Ba atoms are located 3.43 Å from the Cu(1) site and the next Cu(1) atom is located at 3.86 Å. Fourier transformed EXAFS
The Fourier filtered first shell contribution to EXAFS for the \( \text{Au}_2\text{O}_3 \) and \( \text{YBa}_2\text{Au}_{0.3}\text{Cu}_{2.7}\text{O}_{7.6} \). The first shell contribution was obtained by back-transforming the region marked by vertical lines in figure 4. The \( \chi(k) \) term does not decrease as rapidly for \( \text{Au}_2\text{O}_3 \); this can be attributed to the rapid decrease in backscattering amplitude of the oxygen nearest neighbors. The static Debye-Waller term may also serve to diminish the EXAFS signal at higher \( k \) values. The \( \chi(k) \) term does not decrease as rapidly for \( \text{YBa}_2(\text{Au}_{0.1}\text{Cu}_{0.9})_3\text{O}_{7.6} \), this suggests that the Au-O first shell in 123 is less disordered or has a smaller Debye-Waller factor.

**SUMMARY AND CONCLUSIONS**

XANES and EXAFS features support earlier studies which concluded that small amounts of gold can be incorporated in \( \text{YBa}_2\text{Cu}_{7.6} \) at the Cu(1) site. The gold shows significantly less 5d involvement in the Au-O bond in the superconductor than in \( \text{Au}_2\text{O}_3 \). This could be related to the doping of the oxygen with holes and this is similar to the change in the number of holes on the copper-oxygen component when the material is made superconducting by hole doping. Au has less effect on the superconducting properties than Fe presumably because the gold does not localize holes on itself. There are no obvious changes in the Cu K edge and we conclude that Au substitution has little or no effect on the chemical state of copper or oxygen. Our EXAFS data show that Au is coordinated by oxygen and is in a more ordered environment than \( \text{Au}_2\text{O}_3 \). The lack of a good Au-O standard hinders a more thorough analysis of the Au L\textsubscript{3} EXAFS. The Cu K edge EXAFS is virtually identical to that published for \( \text{YBa}_2\text{Cu}_{3}\text{O}_{7.6} \).

**ACKNOWLEDGEMENTS**

The authors thank Professor M. Croft of Rutgers University for help in obtaining some of the EXAFS data and S. M. Heald, J. Jayanetti, and E. Barrera for help in performing and analyzing the EXAFS and XANES measurements. M. W. R. acknowledges the support of the U.S. Department of Energy, Division of Materials Sciences under Contract No. DE-AC02-CH00016. A. F. H. acknowledges support from the Space Electronics
Division of the NASA Lewis Research Center. The X-11 beamline and the National Synchrotron Light Source are supported by the U.S. Department of Energy. Contracts No. DE-AC05-80-ER10742 and DE-AC02-CH00016, respectively.

REFERENCES


Division of the NASA Lewis Research Center. The X-11 beamline and the National Synchrotron Light Source are supported by the U.S. Department of Energy. Contracts No. DE-AC05-80-ER10742 and DE-AC02-CH00016, respectively.

REFERENCES


XANES and EXAFS Study of Au-Substituted YBa$_2$Cu$_{3}$O$_{7-\delta}$

Mark W. Ruckman and Aloysius F. Hepp

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio  44135-3191

National Aeronautics and Space Administration
Washington, D.C.  20546-0001

Prepared for the Fourth Annual Conference on Superconductivity and Applications sponsored by The New York State Institute on Superconductivity. Mark W. Ruckman, Brookhaven National Laboratory, Upton, New York 11973-5000; Aloysius F. Hepp, NASA Lewis Research Center.

The near-edge structure (XANES) of the Au L$_3$ and Cu K edges of YBa$_2$Au$_{0.3}$Cu$_{2.7}$O$_{7-\delta}$ has been studied. X-ray diffraction suggests that Au goes on the Cu(1) site and XANES shows that this has little effect on the oxidation state of the remaining copper. The gold L$_3$ edge develops a white line feature whose position lies between that of trivalent gold oxide (Au$_2$O$_3$) and monovalent potassium gold cyanide (KAu(CN)$_2$) and whose intensity relative to the edge step is smaller than in the two reference compounds. The L$_3$ EXAFS for Au in the superconductor resembles that of Au$_2$O$_3$. However, differences in the envelope of the Fourier filtered component for the first shell suggest that the local structure of the Au in the superconductor is not equivalent to Au$_2$O$_3$.

XANES; High-temperature superconductivity; Au-doped superconductors; EXAFS; Gold chemistry

Unclassified – Unlimited

Unclassified

10

A02