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Near-Edge Study of Gold-Substituted YBa$_2$Cu$_3$O$_{7-\delta}$

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Abstract

The valence of Cu and Au in YBa$_2$Au$_{0.3}$Cu$_{2.7}$O$_{7-\delta}$ was investigated using x–ray absorption near–edge structure (XANES). X–ray and neutron diffraction studies indicate that Au goes on the Cu(1) site and Cu K–edge XANES shows that this has little effect on the oxidation state of the remaining copper. The Au 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 height relative to the edge step is smaller than in the two reference compounds. The appearance of the Au L$_3$–edge suggests that fewer Au 3d states are involved in forming the Au–O bond in YBa$_2$Au$_{0.3}$Cu$_{2.7}$O$_{7-\delta}$ than in trivalent gold oxide.

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Substitution of many metals in $YBa_2Cu_3O_{7-\delta}$ (abbreviated as 123 in the following)[1-4] reduces the superconducting transition temperature T_c. Metals like Fe, Co, or Al replace linear chain site copper, the Cu(1) site, and depress T_c more slowly than Zn or Ni which replace copper located on the CuO^{2-} planes, the Cu(2) site. X-ray absorption near-edge structure (XANES) studies[5,6] indicate that transition metal substitutions sometimes change the oxidation state of Cu or oxygen. An apparent exception to the above generalization is the behavior of Ag and Au. Considerable amounts of Au or Ag can be put into 123 before T_c begins to decrease.[7] Streitz et al.[8] examined the microstructure of Au/123 composites and found that separate Au and Au-containing 123-like phases existed after heat treatment in oxygen. Hepp et al.[9] and Cieplak et al.[10] investigated $YBa_2(Au_xCu_{1-x})_3O_{7-\delta}$ using x-ray diffraction[9,10] and neutron scattering[10] and found that Au went into the Cu(1) site.

In this communication, we report the results of an examination of the Cu K and Au L_3 x-ray absorption edges for $YBa_2(Au_xCu_{1-x})_3O_{7-\delta}$ designed to determine the valences of Cu and Au. We find that an Au substitution of 8 mole percent has no measurable effect on the oxidation state of Cu in 123 which is divalent. The appearance of the Au L_3 edge suggests that the valence of gold is less in the superconductor than in trivalent Au_2O_3.

Samples used in this study were synthesized and characterized at NASA Lewis Research Center; synthetic details are discussed in reference 9. For $YBa_2(Au_{0.1}Cu_{0.9})_3O_{7-\delta}$, x-ray diffraction (XRD) patterns and x-ray photoemission (XPS) 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

2

structural chemistry of Au (see reference 9 for relevant discussion). Hepp et al.[9] found no evidence for the presence of secondary phases in their x–ray data for Au substitutions less than 10 mole percent. The formation of a second phase was readily detected in the x–ray diffraction data when more than 10 mole percent was put in 123. T_c was observed to be 89 K for the 8 mole percent gold containing material and 91 K for the parent 123 material made without Au_2O_3. It should be emphasized at this point that the x–ray–based results of Hepp et al. have been confirmed by detailed neutron diffraction studies.[10]

The 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 calibrated energy scale. The work was done at the X–11A beamline at the Brookhaven National Synchrotron Light Source (NSLS). The technical details of this beamline are published in reference 11. The resolution of the monochromator is estimated to be ~1.0 eV at the Cu k–edge and ~1.2 eV at the Au L_3 edge. The samples were crushed into powder and screened through 400–mesh before dispersal onto adhesive tape. The near–edge data for the Cu K and Au L_3 edges was obtained and analyzed using standard procedures. A linear background was removed from the edge before normalization. Energy calibration of the edge was ensured by measuring the L_3 edge from a gold foil and the k–edge from a Cu foil simultaneously with the superconducting samples.

The Cu k–edges for the 123 material (solid line) and the 8 mole percent Au sample (dashed line) are shown in figure 1. The shape of the Cu k–edge is complex and several interpretations of it exist.[12-16] XANES results are now available for highly oriented powders or single crystal

3

materials using polarized x-rays and provide the most reliable data for the Cu k edge.[17-20] The Cu k near edge structure arises from dipole transitions from the Cu ls core level to the low-lying copper valence or conduction band states with p or π symmetry and to transitions from the Cu ls 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.[17] examined the Cu k-edge from 123 powders oriented such that the x-ray polarization vector ê 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 oxygen site and the formation of Cu^{1+}.[21,22] Peak "B" is due to transitions from the ls to $4p\pi$ band accompanied by shake down transitions ($4p\pi^*$) and peak "C" contains contributions from the ls to $4p\pi$ and ls to $4p\sigma$ transitions from the Cu(2) and the Cu(1) sites. The feature marked "D" is identified as a shape resonance. Figure 1 shows that the Cu-k edges for $YBa_2Cu_3O_{7-\delta}$ (solid line) and $YBa_2(Au_{0.1}Cu_{0.9})_3O_{7-\delta}$ (dashed line) are virtually identical which indicates that Au substitution has little or no effect on the valence of copper.

The Au L_3 edges for $YBa_2(Au_{0.1}Cu_{0.9})_3O_{7-\delta}$, Au foil, monovalent $KAu(CN)_2$ and trivalent Au_2O_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 $5d_{1/2}$ transitions (white line feature).[23] The L_3 edge also has a contribution from the $2p_{3/2}$ to $5d_{3/2}$ level but it is much weaker than the $2p_{1/2}$ to $5d_{3/2}$ and $2p_{3/2}$ to $5d_{1/2}$ transitions. The intensity of the white line feature is thought to provide a good indication of the 5d occupation.[24] For Au (small dashed curve), the 5d band is filled and no white line feature is observed. The oxidation of Au to the mono or trivalent state creates the white line feature. We find that the white line area is larger for Au_2O_3 (dot–dashed line) than $KAu(CN)_2$ (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_2O_3 and $KAu(CN)_2$ is less than the ratio of d–electron removal suggested by the valence. The white line area for Au in 123 (solid line) is considerably smaller than either of the reference compounds and lies at lower photon energy than $KAu(CN)_2$ but at a higher photon energy than Au_2O_3.

The Au L_3 near edge data for $YBa_2(Au_{0.1}Cu_{0.9})_3O_{7-\delta}$ suggests that the valence of Au in the 123 material differs from that of Au in trivalent Au_2O_3. Iron also replaces Cu on the chain site and is trivalent. However, the substitution of 8 mole percent Fe depresses T_c by 55 K[25] rather than the 2 K found for the equivalent gold substitution. Yang et al.[5] found that Fe substitution modifies the O k–edge and reduces the number of 2p holes on the oxygen. We suggest, based on the reduction in the apparent number of unoccupied Au 5d states for the Au–O bond in 123, when compared to Au_2O_3 and the small Au–induced change in T_c, 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_c material becomes oxygen deficient and holes

5

are removed from the oxygen site. [21]

The near-edge data suggests that small amounts of Au incorporated in 123 at the Cu(1) have less 5d involvement in the Au–O bond in the superconductor than in Au_2O_3. We believe this is related to the doping of the oxygen site with holes. Gold has less effect on the superconducting properties than Fe presumably because Au does not localize the 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 Cu or oxygen.

Acknowledgment

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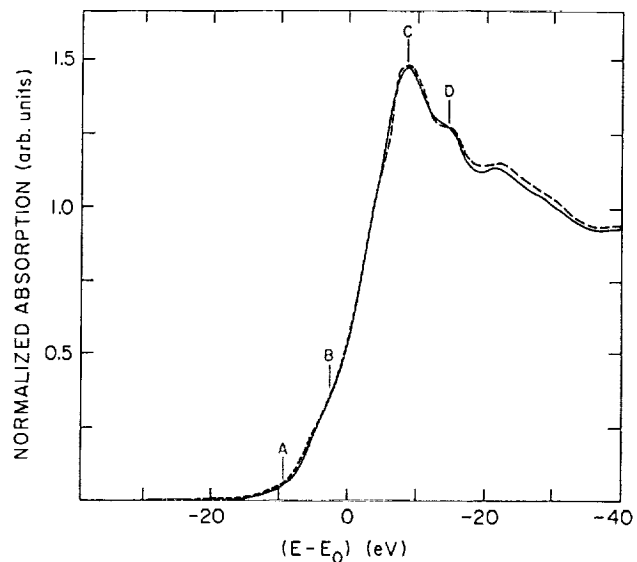Figure 1.–Cu k-edge XANES for $YBa_2Cu_3O_{7-\delta}$ (solid curve) and $YBa_2Au_{0.3}Au_{2.7}O_{7-\delta}$ (dashed curve). The energy reference was maintained using a Cu foil.
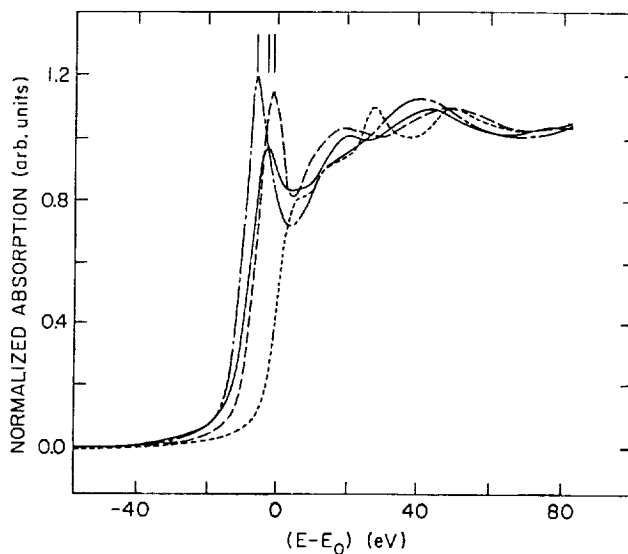

Figure 2.–Au L_3 absorption edges for gold (dotted curve), a monovalent gold compound - $KAu(CN)_2$ (dashed curve), trivalent gold oxide - Au_2O_3 (dot-dashed curve) and $YBa_2Au_{0.3}Au_{2.7}O_{7-\delta}$ (solid). A consistant energy reference was maintained by examining the L_3 edge of a gold foil simultaneously with these samples.

9

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The valence of Cu and Au in $YBa_2Au_{0.3}Cu_{2.7}O_{7-\delta}$ was investigated using x-ray absorption near-edge structure (XANES). X-ray and neutron diffraction studies indicate that Au goes on the Cu(1) site and Cu K-edge XANES shows that this has little effect on the oxidation state of the remaining copper. The Au L_3 edge develops a white line feature whose position lies between that of trivalent gold oxide (Au_2O_3) and monovalent potassium gold cyanide ($KAu(CN)_2$) and whose height relative to the edge step is smaller than in the two reference compounds. The appearance of the Au L_3-edge suggests that fewer Au 3d states are involved in forming the Au-O bond in $YBa_2Au_{0.3}Cu_{2.7}O_{7-\delta}$ than in trivalent gold oxide.

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