## Electronic structure changes and superconductivity in $YBa_2Cu_3O_{7-x}$

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X-ray photoelectron spectroscopy (XPS) studies were performed on bulk polycrystalline samples of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> as a function of temperature through the superconducting transition. With decreasing temperature, clear changes were observed in the photoelectron spectrum which can be interpreted as signatures of the Cu<sup>3+</sup> and perhaps the Cu<sup>1+</sup> oxidation states, in addition to the usual Cu<sup>2+</sup> state. These changes were not observed in samples which had been rendered nonsuperconducting by baking in vacuum. These results may have implications for the mechanism for superconductivity in this high- $T_c$  compound.

X-ray photoelectron spectra of high- $T_c$  superconductors such as YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> have been investigated by a number of workers<sup>1-8</sup> in order to ascertain the electronic structure of this material, and to learn something about the mechanism for its superconductivity. This is of interest because the weakness of the isotope effect in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> suggests<sup>9</sup> that the phonon mechanism may not be the cause of its superconductivity. Theoretical approaches to high-temperature superconductivity have fallen into several categories involving either the replacement of the phonons of the conventional theory by some other Bose-like excitation,<sup>10</sup> the use of variants of the resonating valence-bond approach,<sup>11</sup> or the consideration of the special role of oxygen defects.<sup>12</sup>

Electronic structure studies such as x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and resonant photoemission have, thus far, been largely inclusive <sup>1-8,13</sup> in establishing the presence of the Cu<sup>3+</sup> oxidation state which is nominally present<sup>14</sup> and important for some theories. Here we report studies of the temperature dependence of the x-ray photoelectron spectrum of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> from 300 K down to temperatures below the superconducting transition. We have concentrated on the study of spectra associated with the core levels of Cu and O atoms since these two elements appear to play a critical role in superconductivity at high temperatures. Our major finding is a change in the Cu core-level spectrum which appears to be consistent with the gradual increase with decreasing temperature of the Cu<sup>3+</sup> oxidation state. Other features of the data are consistent with a gradual increase in the Cu<sup>1+</sup> oxidation state reported in Ref. 8.

The bulk polycrystalline samples of  $YBa_2Cu_3O_{7-x}$  used in this study were prepared in the standard manner, using solid-state reaction techniques. The onset of the superconducting transition was observed to be 94 K with zero resistance being achieved at 88 K. Photoelectron spectra were obtained using a Perkin-Elmer/Physical Electronics

Model 555 equipped with a Mg  $K\alpha$  source (1253.6 eV) and a double-pass cylindrical mirror analyzer (CMA). For high-resolution spectra, the CMA was operated in a retarding mode with a pass energy of 25 eV. The vacuum system, which had a base pressure of  $5 \times 10^{-10}$  Torr, was equipped with a rapid sample introduction system with the introduction rod having a liquid-nitrogen-cooled sample mount. Measurements were made with the sample temperature stabilized at the reported temperature. It was possible to acquire spectra within a few minutes of sample introduction into ultrahigh vacuum (UHV)  $(1 \times 10^{-9} \text{ Torr})$  and within 45 min of introduction into high vacuum  $(5 \times 10^{-5} \text{ Torr})$ . This quick analysis time subsequent to sample insertion into vacuum avoided the effects of sample degradation due to oxygen loss. This degradation almost certainly occurs as a decrease by several percent of the intensity of the O(1s) peak relative to the intensities of various Cu, Y, and Ba photoelectron peaks was observed after only 3-4 h for a sample in UHV at room temperature.

For each experiment, the sample was scraped to expose a fresh surface before insertion into the vacuum system. This procedure is different from the standard practice in photoemission experiments in which the sample surfaces are cleaned in situ to avoid uncertainties of atmospheric exposure. An alternative protocol was developed to deal with this limitation of our facilities. A control experiment was carried out on samples rendered nonsuperconducting by heat treatment in vacuum (700°C for 24 h). These nonsuperconducting samples were cut from samples that were originally superconducting. X-ray diffraction studies showed that after heat treatment, the structure was tetragonal rather than an orthorhombic. Also, the measurement of R(T) showed semiconducting behavior with no trace of superconductivity down to 4.2 K. These heattreated samples were exposed to air for several days before being measured to ensure that they were processed in a manner identical to the superconducting samples.

The electrical resistance of the samples was monitored in situ during the acquisition of spectra using a four-probe dc method. In the course of these measurements, the polarity of the current was reversed regularly to rule out any dc offsets such as might result from thermoelectric effects. Sample temperatures were obtained from the measured sample resistance using as a calibration the results of prior measurements of R(T) carried out in a separate apparatus. The superconducting transition was observed in an unambiguous manner in orthorhombic samples in these in situ resistance studies. For samples described as being at temperatures below  $T_c$  where their resistance is zero, there is naturally an uncertainty in the temperature, with T being in the range 77 K < T < 88 K. In each instance, photoelectron spectra and electron energy-loss spectra were obtained with the sample temperature stabilized at the reported temperature as determined from measurements of resistance. In other words, data were acquired with the sample in thermal equilibrium with the temperature fixed. When the sample was warmed back to 300 K after each low-temperature measurement, the changes in the spectra observed at low temperatures disappeared.

There are difficulties in interpreting p-shell spectra for the transition elements due to a high sloping background which is a consequence of secondary electrons and effects



FIG. 1. Copper  $2P_{3/2}$  core-level spectra of (a) superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (o-YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>), and (b) nonsuperconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (t-YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>) at 300 K and 77 K < T < 88 K.

resulting from inelastically scattered photoelectrons. To obtain a genuine photoelectron signal free of these effects, spectra were deconvoluted with electron energy-loss spectra.<sup>15</sup> The deconvolution routine also corrected broadening due to the achromaticity of the x-ray source and the finite analyzer resolution.

Deconvoluted Cu(2P) core-level spectra of both orthorhombic and tetragonal samples at 300 K, and at a temperature the order of 80 K (below  $T_c$ ), are shown in Fig. 1. Comparing with CuO core-level spectra, <sup>16</sup> we find the majority oxidation state of the Cu atoms to be Cu<sup>2+</sup>. The main Cu(2P<sub>3/2</sub>) peak at 933.8 eV and the Cu(2P<sub>1/2</sub>) peak at 954 eV are of  $d^{10}$  final-state character where electrons are transferred from a ligand to Cu to fill a shell. The satellites, found at about 942 and 963 eV, which are of  $d^9$ final-state character, exhibit multiplet splitting due to the interaction between a Cu(2P) core hole and an unpaired electron in the 3d shell.

There are significant changes in the shape of the spectra of the superconducting compound with decreasing temperature. The main peaks, although found at approximately the same position, exhibit, with decreasing temperature, increased spectral strength at higher binding energies with the lower energy side almost unchanged. The temperature dependences of the full width at half maximum (FWHM) of the  $Cu(2P_{3/2})$  peaks of orthorhombic (superconducting) and tetragonal samples together with CuO spectrum are given in Fig. 2. The gradual changes of the FWHM with temperature in the case of superconducting samples can be clearly seen, whereas the FWHM of the nonsuperconducting samples and of CuO remain virtually unchanged. Dauth et al.<sup>7</sup> have reported the same changes in Cu core spectra of in situ cleaned superconducting  $YBa_2Cu_3O_{7-x}$  with decreasing temperature (see Fig. 3 of Ref. 7).

The enhancement of the spectral strength at higher binding energy of the  $Cu(2P_{3/2})$  peak as T is reduced can be interpreted as evidence of an increase in the fraction of copper atoms in the Cu<sup>3+</sup> oxidation state at low tempera-



FIG. 2. Temperature dependence of the full width at half maximum (FWHM) of  $Cu(2P_{3/2})$  main peaks of the o-YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, t-YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, and CuO.

tures relative to 300 K as it takes more energy to create a hole in an atom the larger its positive charge (or oxidation state).<sup>17</sup> This interpretation is supported by the recent work of Steiner *et al.*<sup>5</sup> who measured  $Cu(2P_{3/2})$  core-level spectra of NaCuO<sub>2</sub> in which copper is claimed to be in the  $Cu^{3+}$  state. Using these data, synthetic copper core-level spectra of a material containing combinations of the divalent CuO and trivalent NaCuO<sub>2</sub> with composition given by  $(1-y)CuO + yNaCuO_2$  were constructed. These spectra exhibited increasing spectral strength at higher binding energies of the  $Cu(2P_{3/2})$  peak with increasing y, the relative amount of NaCuO<sub>2</sub> in a manner similar to the shift with decreasing temperature in the  $Cu(2P_{3/2})$  spectrum of superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (see Fig. 3 of Ref. 5).

Granting the existence of the Cu<sup>3+</sup> state in superconducting  $YBa_2Cu_3O_{7-x}$ , one might ask where the electrons go and how charge balance is provided. One possibility is a concurrent enhancement of the  $Cu^{1+}$  state. Evidence of this is the fact that the ratios of the intensities of the satellites relative to the main  $Cu(2P_{3/2})$  peak are smaller at low temperatures than at 300 K, a fact also noted in Ref. 8 and discussed in detail there. The satellites found for the  $Cu^{1+}$  state in other systems are known to be much smaller than those for  $Cu^{2+}$ .<sup>5,16</sup> Thus, any tendency towards larger satellite intensity such as might be associated with the Cu<sup>3+</sup> state may have been overwhelmed by the tendency towards a smaller satellite in the Cu<sup>1+</sup> state.<sup>16,18</sup> Additional evidence of  $Cu^{1+}$  is a change in the shape of the Auger spectra of the  $Cu(L_3VV)$  transition which is shown in Fig. 3. What is seen is a shift in the line from its position at 916.6 eV at 300 K to 915.0 eV at low temperatures. Similar results are also found in Ref. 8. Comparing the magnitude of the shift with the differences of the Auger spectra of the same transition in CuO (918.2 eV) and Cu (916.7 eV) (Ref. 16), it is reasonable to attribute the effective shift in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> with decreasing temperatures to a reduction of the oxidation state of some of the copper atoms from  $Cu^{2+}$  to  $Cu^{1+}$ . This conjecture would be consistent with the kinetic energy of the Auger electrons being dominated by the 2P core energies which would be lower for  $Cu^{1+}$  than for  $Cu^{2+}$ . The overall broadening of the Auger peak may be sufficient to accommodate the simultaneous contributions from Cu<sup>1+</sup>, Cu<sup>2+</sup> oxidation states. The nonsuperconducting tetragonal phase  $YBa_2Cu_3O_{7-x}$  showed no noticeable changes in its Cu core-level spectra and  $Cu(L_3VV)$  Auger transition with temperature, but its main Cu  $(2P_{3/2})$  peak was located at a lower binding energy and exhibited a smaller satellite intensity than the superconducting orthorhombic phase. This is consistent with the reduction of the oxidation state which would accompany oxygen removal.

In considering further details of the electronic structure below 300 K, it is useful to note the suggestion of Sarma, Speedhar, Ganguly, and Rao<sup>1</sup> who observed the development of an O<sub>2</sub> peak (533.3 eV) on cooling to low temperatures which was interpreted as the dimerization of the oxygen atom in superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>. Although we have observed similar changes in O(1s) core-level spectra on cooling, it appears that these changes may not be associated with the superconductivity of the sample.



FIG. 3. Copper Auger transition  $(L_3VV)$  spectra of (a) o-YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, and (b) t-YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> at 300 K and 77 K < T < 88 K.

First, the effect is also observed in nonsuperconducting samples. Second, the  $O_2$  peak grows with *time*, in contrast with the changes in the various Cu peaks, which were time independent. The latter implies the the effect is due to oxygen molecule overlayers on the surface of the superconductor and is unrelated to any electronic structure change in the material itself. Because a fresh surface of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> was not prepared in situ, we cannot unequivocally exclude the possibility of a much smaller signal due to dimerization of oxygen atoms intrinsic to the material, and related to superconductivity, in addition to the larger signal clearly associated with adsorbed oxygen on the surface. The fact that adsorbed oxygen on a Cu metal surface stays mostly in atomic form above 150 K and forms molecules below 150 K is a possible explanation of why the  $O_2$  peak and not the O peak grows as the temperature is lowered.<sup>19</sup>

In order to determine the effect of the above  $O_2$  overlayers on the Cu spectra, independent measurements on samples of pure CuO and tetragonal YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> were performed. Both O<sub>2</sub> and H<sub>2</sub>O were introduced separately into the vacuum chamber while samples were held at low temperature. It was found that the Cu(2P) peaks and the Cu(L<sub>3</sub>VV) Auger peaks remained unchanged within the resolution limit of the analyzer while the corresponding peaks in the O(1s) core-level spectra changed with the amount of  $O_2$  and  $H_2O$  introduced. If the tetragonal samples were dosed with either  $O_2$  or  $H_2O$ , then the growth of a peak at the location of the  $O_2$  peak of the orthorhombic samples was observed. This fact is consistent with the previous observation that time-dependent increase of the  $O_2$  peak was due to adsorption.

In summary, we find that the photoelectron spectra of Cu core levels and the Auger spectra associated with the  $Cu(L_3VV)$  transition in superconducting  $YBa_2Cu_3O_{7-x}$  samples exhibit significant changes on cooling from 300 K down to temperatures below  $T_c$ . These changes were not observed in tetragonal samples rendered nonsuperconducting by removal of oxygen, and processed in an identical manner to the orthorhombic, superconducting samples. The data thus far suggest the presence of the  $Cu^{3+}$  and perhaps the  $Cu^{1+}$  oxidation states at low temperatures in superconducting samples, a result which would have important implications for theoretical models of the superconductivity of  $YBa_2Cu_3O_{7-x}$ . The presence of these oxidation states would not at all be evident in our data at 300 K without a detailed multiparameter analysis.

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Recent x-ray absorption studies  $^{20}$  have been interpreted as indicating the presence of copper in the Cu<sup>3+</sup> state, even at 300 K.

Studies of the oxygen core-level spectra indicate that the sample surfaces are contaminated by air. The adsorbed layer must certainly reduce the signal-to-noise ratio of all of the spectra and probably would have a direct effect on them. On the other hand, an adsorbed layer should not influence changes of the spectra with temperature differently for the superconducting and nonsuperconducting samples.

The authors would like to thank B. Koepke of Honeywell and C. Gallo of 3M for providing samples. They would like to thank Dr. D. Hawn for supplying the deconvolution program and R. Haasch for actually doing the deconvolutions. We would also like to thank R. Caretta of the Surface Analysis Center at the University of Minnesota for his assistance. This work was supported by the Air Force Office of Scientific Research under Grant No. 87-0372.

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