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Interaction of H_2O with a high-temperature superconductor

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The effect of water on the high-temperature superconductor $YBa_2Cu_3O_7$ has been studied. Photoemission measurements show that water modifies valence-band states, reduces the number of inequivalent Ba sites, and induces O 1*s* core-level components at 534 and 531 eV. The 534-eV core-level component is coincident with that of cryosorbed ice and the enhanced 531-eV component is due to a new water-induced bonding environment in the superconductor; this is most probably a hydroxyl species. Changes in the Ba core-level appearance suggest that water may be preferentially modifying YBa_2CuO_7 in a way that affects the Ba atomic environment. The effect of water on superconductivity and its possible implications for bulk superconducting transport in ceramics are discussed. Previous reports suggesting oxygen dimerization below T_c, as well as other reported changes in the spectrum, are improbable in view of these present results.

Since the discovery of high-temperature superconductivity in the perovskites $La_{2-x}Ba_xCuO_4$ (Ref. 1) and $YBaCu_3O_7$ (Ref. 2) there have been a number of experimental studies of their different properties.[3] It has been determined that the bulk crystal structure,[4] number of oxygen vacancies,[5] and chemical composition play a crucial role in the high-T_c phenomenon. Surface studies such as photoemission,[6] inverse photoemission,[7] and mass spectroscopy[8] have indicated that this complex material is highly reactive. Adsorption of metal overlayers[9] is now known to irreversibly change the chemistry of both freshly scraped and fractured surfaces. Water also reacts vigorously with the bulk materials producing a nonsuperconducting material, O_2 gas, CuO, and $Ba(OH)_2$ (Ref. 10). Smaller amounts of water may have an impact on the stability of interfaces formed between these superconductors and dissimilar materials.

In this paper, we examine the interaction of water with $YBa_2Cu_3O_7$ on an atomic level as a function of temperature. Synchrotron radiation has been used to probe the modification of the valence-band and shallow binding-energy core levels. X-ray photoemission (XPS) was used to monitor the O 1*s* and Cu $2p^{3/2,1/2}$ core levels, to identify the number of inequivalent oxygen-bonding sites, and to determine the copper valence. Our study shows that the adsorption of monolayer amounts of water chemically modifies the surface or selvedge in a well-defined manner and we conclude that similar modifications in the grain boundaries may have influenced earlier measurements of the resistivity in these materials at higher temperatures in the region of 240 K. The adsorption of other chemically active gases (e.g., H_2, CO, and O_2), which will be discussed elsewhere, did not induce similar chemical effects in the material and hence we believe that water plays a unique role in the surface modification.

Synchrotron-radiation-based photoemission and XPS measurements were performed, on the U7B beam line at the National Synchrotron Light Source (NSLS), in a UHV chamber equipped with a flow through liquid-He cryostat capable of reaching 4.2 K. Measurements with a surface-mounted diode demonstrated that surface temperatures near 20 K were achieved. The $YBa_2Cu_3O_7$ sample was a polycrystalline single-phase sample with a sharp superconducting transition near 93 K. The sample was scraped *in situ* under UHV conditions with an alumina grinder. This procedure produced a surface that was free of aluminum but which showed evidence for at least two inequivalent oxygen-bonding environments.[11] Water was admitted to the vacuum chamber using a gas doser and attenuation of substrate photoemission features suggested that approximately 5–7 H_2O monolayers cryosorbed on the substrate.

In Fig. 1, valence-band photoemission spectra between 50 and 150 eV are shown for clean $YBa_2Cu_3O_7$ at 20 K [Fig. 1(a)] and for the same surface following the adsorption and desorption of water [Fig. 1(b)]. The spectra have been normalized to equivalent count rates to facilitate comparison. The spectra at low photon energies emphasize the oxygen-derived components.[12] Exposure to water has an irreversible effect on the valence-band structure of $YBa_2Cu_3O_7$ and induces a new state marked (4) at 9.4 eV binding energy. Only weak intensity is observed at this energy for the freshly scraped sample, in contrast to previous reports. This new feature displays oxygen character, decreasing in intensity relative to the Cu 3*d* valence-band states as the photon energy is increased.[6] Exposure of metal oxides[13,14] to water often shows peaks in this energy range that can be attributed to chemisorbed H_2O or OH^- species. The O 1*s* spectra discussed below allow us to conclude that this peak is the OH_σ orbital as-

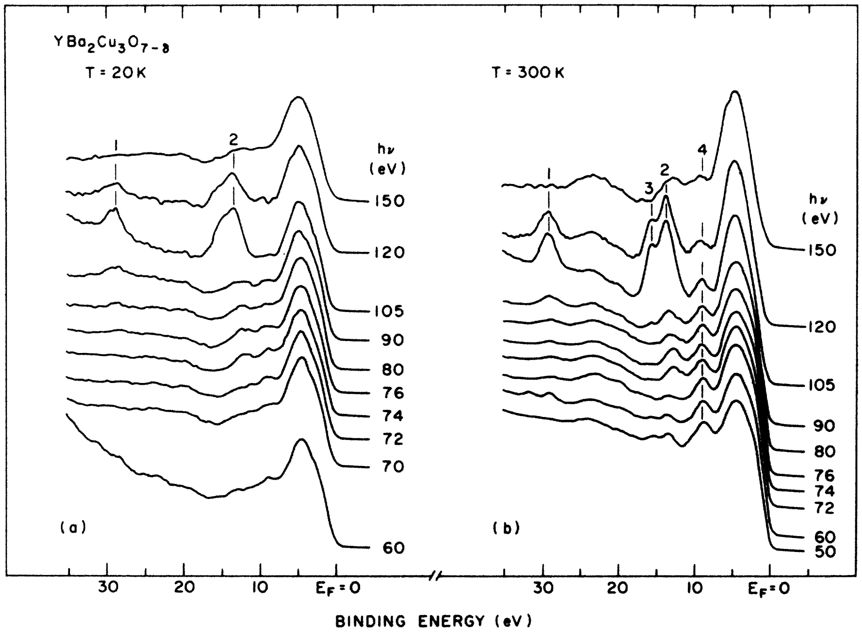

FIG. 1. (a) Photoemission spectra for freshly scraped $YBa_2Cu_3O_7$ at 20 K. Barium 5*s* and 5*p* peaks are labeled (1) and (2), respectively. (b) Spectra for the same surface after 5–7 ML H_2O had been adsorbed at 20 K and thermally desorbed by warming to 300 K. The resolved Ba $5p^{3/2}$ and $5p^{1/2}$ are labeled (2) and (3). A H_2O-induced feature at 9.4 eV is labeled (4).

sociated with hydroxyl species absorbed on the surface or incorporated in the bulk. The corresponding OH_π level should be found in the valence-band region[15] and the O 2*s* level is observed at 24 eV binding energy.

In Fig. 2, photoemission spectra for the unmodified, modified, and ice covered $YBa_2Cu_3O_7$ surface are shown. Following exposure to water at 20 K peaks attributable to $2a_1$ (−27 eV), $1b_2$ (−12 eV), $3a_1$ and $1b_1$ (6–8 eV) molecular orbitals[16] are identifiable. As the temperature of the surface is raised from 20 K to room temperature, we observe in Fig. 2 that the emission derived from the O 2*s* orbital, the $2a_1$ peak in physisorbed molecular H_2O, shifts from 27 eV with respect to the Fermi level to a binding energy at 24 eV. This shift we associate with dissociation of the water molecule or formation of a surface hydroxide. As previously noted this transition is accompanied by the appearance of the OH_σ feature at a binding energy of 9.4 eV.

In the clean spectra of $YBa_2Cu_3O_7$ a Cu 3*d* satellite is observed at 12.5 eV binding energy, this is most easily seen in the spectra for photon energies above and close to the Cu 3*p* threshold, at 72 eV [Fig. 1(a)]. The position of this satellite is close to that found for CuO (12.9 eV); the satellite in Cu_2O is at 15.3 eV (Ref. 17). Following the reaction with H_2O, the satellite shifts to 1 eV higher binding energy indicating a modification of the copper electronic environment. However, the more bulk sensitive XPS studies of the Cu 2*p* core levels[18] show little or no change in their satellite structure, which can also be related to the copper valence. This indicates that the changes are in the surface region. Interaction of $YBa_2Cu_3O_7$ with water also affects the electronic environment of barium. Before water exposure [Fig. 1(a)], the shallow Ba $5p^{3/2,1/2}$ and 5*s* core levels, which are resonantly enhanced at the 4*d* threshold near 100 eV photon energy, appear less distinct. The overall appearance of these Ba core levels [Fig. 1(a)] suggests that some disorder, either structural or electronic, creates a number of inequivalent but closely spaced Ba core levels. As has been found in earlier studies of the perovskite oxide $SrTiO_3$ (Ref. 14), it is highly likely that defect sites in the surface region lead to a different potential at the Ba site. Introduction of water [Fig. 1(b)] causes the barium levels to become much sharper with an apparent shift to higher binding energy. The $5p^{3/2}$ and $5p^{1/2}$ can be clearly resolved and the 5*s* level becomes narrower. The spectroscopic data suggest that the Ba environment becomes more homogeneous. It is possible that Ba could be removed from the matrix to form a single-phase barium compound [e.g., $Ba(OH)_2$] but the lack of change in the relative areas of the Ba peaks relative to the Cu-O valence states indicates that Ba is probably not being substantially removed from the superconducting compound.

More evidence for the chemical reaction of H_2O with $YBa_2Cu_3O_7$ can be observed in the behavior of the O 1*s* core levels. Figure 3 shows the O 1*s* core level of the freshly scraped superconductor at 20 K both before and after adsorption of ∼5–7 ML of H_2O. The clean surface shows peaks at 529 and 531 eV with the 529-eV peak approximately six times larger than the 531 peak. A peak at 531 eV has commonly been attributed in previous studies of water-exposed oxide surfaces to the formation of hydroxyl species.[19] The feature at 529 eV has been seen in spectra reported elsewhere and for both $YBa_2Cu_3O_7$ (Refs. 9, 11, and 18) and $La_{1.85}Sr_{0.15}CuO_4$ (Refs. 11 and 20), and can be attributed to the bulk phase. Water adsorption generates a peak at 534 eV binding energy consistent with that reported for water.[21] Indeed studies of

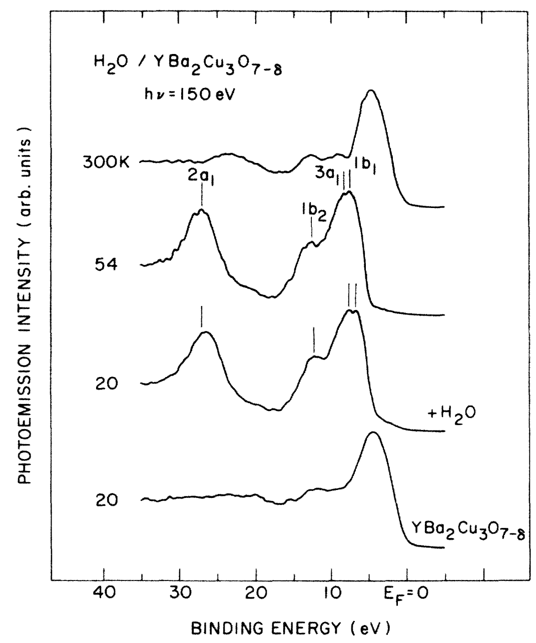

FIG. 2. Valence-band spectra with $h\nu = 150$ eV showing the adsorption of solid water on the superconductor at 20 and 54 K, the dry $YBa_2Cu_3O_7$ surface (bottom), and the H_2O modified YBa_2Cu_3O surface (top).

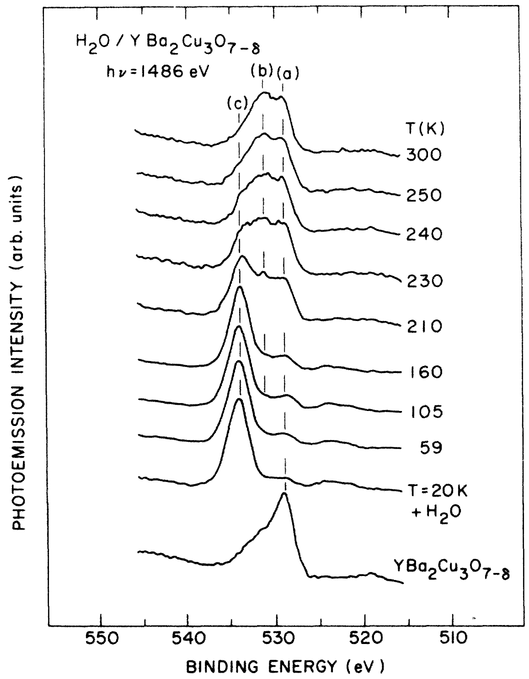

FIG. 3. XPS spectra (Al $K\alpha$ 1486 eV) for dry $YBa_2Cu_3O_7$, the H_2O covered surface at 20 K, and at selected temperatures during the warm-up cycle. O 1*s* binding states at 529, 531, and 534 eV are marked (a), (b), and (c), respectively. The origin of these different peaks is discussed in the text.

H_2O adsorption on nickel oxide surfaces[22] showed the generation of the same "three-peak" structure. The 529-eV peak was identified as characteristic of the oxide O^{2-} structure, the 531-eV peak was associated with oxygen in a hydroxide OH^- species, and the 534-eV peak with molecular water.

Spectra recorded from the superconductor as functions of temperature are shown in Fig. 3. Solid water remains on the surface until the temperature exceeds 160 K. Some small losses of water do occur below 160 K as evidenced by the intensity increase of the substrate derived 529-eV O 1*s* component. The rapid intensity loss of the 534-eV water peak starts when the vapor pressure of ice exceeds 10^{-8} Torr at 160 K (Ref. 23). At 210 K, most of the water ice has gone but sufficient water remains on the surface to produce a peak at 534 eV which is comparable in area to the 529- and 531-eV peaks. The removal of the last significant amount of unreacted surface water occurs only when the temperature exceeds 240 K. In fact, possibly coincidentally, a water peak was observed on the residual gas analyzer in the vacuum chamber as the sample temperature rose through 240 K.

After the water is removed the O 1*s* core level (300 K) again shows the two components at 529 and 531 eV but the 531-eV feature has increased significantly and is now larger than the 529-eV peak. Rescraping the sample removes most of the material which gives rise to the 531-eV peak.

Our data for the interaction of H_2O and $YBa_2Cu_3O_7$ shows that the surface can be irreversibly modified by water adsorption at cryogenic temperatures. The amount of water is estimated to be a few monolayers. We believe our result has important implications for the bulk superconductors because it is likely that sufficient amounts of water could enter into the bulk via grain boundaries or surface layers to cause a modification of the electronic properties of material in these areas. If this modified material is "normal" or has a depressed T_c, the linking of superconducting grains by Josephson tunneling could be disrupted and this would serve to limit the critical current.[24,25]

We note that water- or hydroxyl-induced modification of the surface mimics some of the behavior used to support the conjecture that oxygen dimerizes below T_c. For example, Sarma *et al.*[26] report O 1*s* core-level spectra that show the evolution of a peak at 533.3 eV binding energy and the decrease of a peak at 528.7 eV attributed to the superconducting oxide. Valence-band spectra are also shown which suggest that some adsorbed overlayer must reside on the surface. In other experiments conducted concurrently with this work, we found that H_2O exposures of ~ 0.1 L (1 langmuir = 1 L = 10^{-6} Torr sec) were sufficient to modify the valence band and produce a measureable 534-eV feature. Therefore, we do not believe that our data show any evidence of oxygen dimerization, and we argue that reports of dimerization must be carefully examined to rule out the influence of water. Lastly we wish to draw attention to the fact that the last traces of water seem to be removed from the surface layer at 240 K. This suggests that water could become more mobile and could also be transported to or from the grain boundaries. In light of reports of various transport and physical anomalies at 240 K (Refs. 27 and 28), and possible improvement in T_c by thermal cycling to 240 K (Ref. 29), the possibility that water could play a role in this phenomena should be seriously considered.

In conclusion, this study provides evidence that $YBa_2Cu_3O_7$ can be modified by water at cryogenic temperatures and suggests that a OH^- species may be incorporated in the superconductor. This OH^- species most probably reacts with the oxygen vacancies and modifies both the Ba and Cu electronic environments. We find that most of the water desorbs between 160 and 210 K but a small amount may also preferentially desorb near 240 K. This work illustrates the problem that unintentional water incorporation may have on devices employing interfaces between $YBa_2Cu_3O_7$ and a dissimilar material or the bulk material prepared by ceramic techniques. Reports of dimerization and other reported changes with temperature must be reexamined in view of the effect of water on the surface.

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