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Photoemission study of $YBa_2Cu_3O_7$ through the superconducting transition: Evidence for oxygen dimerization

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Photoemission spectra of $YBa_2Cu_3O_{7-\delta}$ in the normal and superconducting states provide direct evidence for dimerization of oxygen below T_c. Cu^{2+} is found to reduce to Cu^{1+} concomitantly. These changes may be of vital importance to the mechanism of high-temperature superconductivity.

The high-temperature superconductivity of $YBa_2Cu_3O_{7-\delta}$ with zero resistance at ~90 K (Refs. 1–3) has created a great sensation. Besides having the highest T_c of all superconducting oxides known hitherto, this oxide also shows a total Meissner effect.[4] Although many models have been proposed recently for high-temperature superconductivity,[5–7] there is no clear-cut experimental evidence to favor one model over the others. In order to obtain valuable information about the electronic structure of these oxides, which may help to understand the mechanism of superconductivity, we have carried out photoemission experiments on $YBa_2Cu_3O_{7-\delta}$ both in the normal and in the superconducting states. We have found remarkable changes in the valence band as well as the core-level spectra when the oxide goes through the superconducting transition.

$YBa_2Cu_3O_{7-\delta}$ was prepared by heating the mixture of the component oxides at 1200 K for 12 h, followed by heating in oxygen atmosphere at 1100 K for 36 h, in the form of a pellet. The sample was found to be superconducting (zero resistance) at 90 K with a transition width of 3 K. Photoelectron experiments were carried out with a commercial VG ESCA3 Mark II spectrometer. (ESCA denotes electron spectroscopy for chemical analysis.) X-ray photoelectron spectra (XPS) were recorded with Mg $K\alpha$ radiation ($h\nu$=1253.6 eV) with an overall resolution of 0.8 eV. Ultraviolet photoelectron spectra (UPS) were recorded with HeI ($h\nu$=21.2 eV) and HeII ($h\nu$=40.8 eV), respectively, with resolution better than 0.1 eV. Surface cleaning of the sample was performed by *in situ* scraping with a stainless-steel blade at a vacuum of $(5-7)\times10^{-10}$ Torr. The sample was found to contaminate slowly over a period of time, as indicated by a rise in the O(1*s*) peak at 531.3 eV binding energy (see later in the text). This necessitated periodic scraping of the sample. We avoided heating the sample, as heating in vacuum could lead to an oxygen-deficient sample which is not superconducting.

In Fig. 1(a) we show the XPS valence bands of $YBa_2Cu_3O_{7-\delta}$ at 300 and 80 K. Since the cross section of Cu(3*d*) states dominate the spectra at the Mg $K\alpha$ photon energy, we find a low density of Cu(3*d*) states at the E_F for this oxide at both the temperatures. Comparing the spectra at 300 and 80 K, we find a small decrease in the intensity in the energy range between 3.5 and 7.5 eV at 80 K.

In order to understand this change further, we have recorded the HeII spectra of the oxide at 300 and 80 K [Fig. 1(b)]. The spectral features in UPS are dominated by O(2*p*) derived states due to cross-section differences.[8] At both temperatures, we find a low density of O(2*p*) states at the E_F. Comparing the x-ray and uv photoelectron spectra at 300 K, we also find extensive overlap of Cu(3*d*) and O(2*p*) states. More importantly, we find a prominent decrease in the spectral intensity in the energy range of <7.5 eV at 80 K as found in XPS. However, the magnitude of the decrease in intensity is much greater than in XPS. Simultaneously we find a significant increase in the spectral intensity in the energy range of >8 eV at 80 K. Similar results are also obtained with HeI ra-

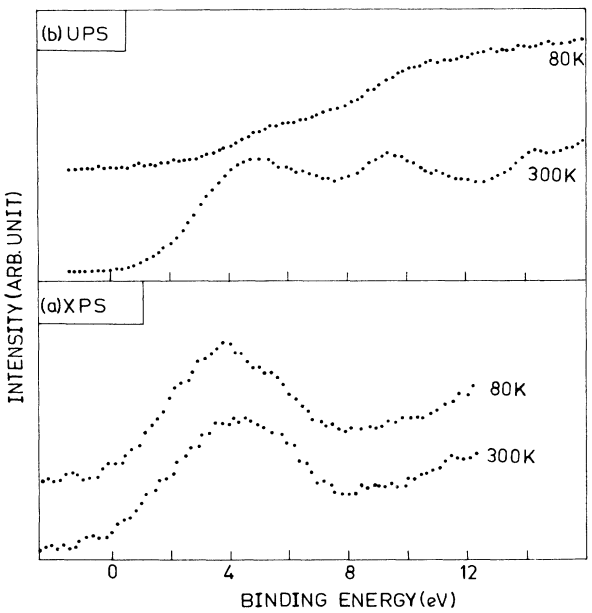

FIG. 1. Photoemission spectra of the valence-band region in $YBa_2Cu_3O_{7-\delta}$ at 300 and 80 K with (a) $h\nu$=1253.6 eV and (b) $h\nu$=40.8 eV.

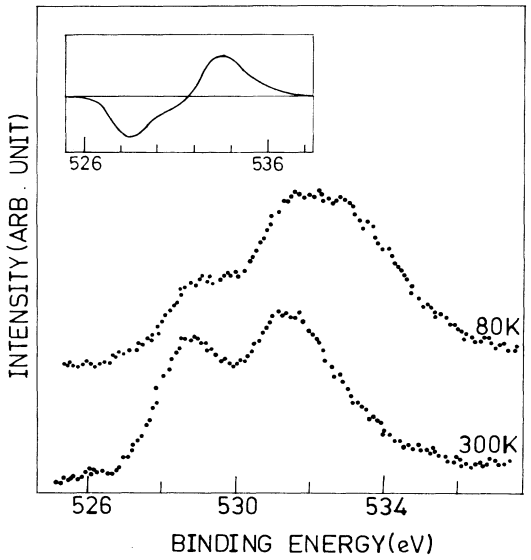

FIG. 2. XPS of O(1s) in $YBa_2Cu_3O_{7-\delta}$ at 300 and 80 K. The inset shows the difference between the spectra recorded at 80 and 300 K.

diation. These changes in the valence-band region can be attributed to a redistribution of O(2p) derived states towards the higher binding energy in the superconducting state. Considering the typical spectral features observed in the molecular adsorption of oxygen on transition metals such as Cu,[9] we suggest that the changes in the spectra seen in Figs. 1(a) and 1(b) are due to dimerization of oxygen ions in this oxide at low temperatures.

If this interpretation is correct, we should see corresponding changes in the O(1s) spectra as well. In Fig. 2 we show the O(1s) spectra recorded at 300 and 80 K. The peak at 531.3 eV is attributed to contaminant species (possibly hydroxyl ions), whereas the peak at 528.7 eV is due to O^{2-} ions. In the 80-K spectrum we see clear evidence of a peak at 533.3 eV which evolves at the expense of the oxide species at 528.7 eV. The binding energy of the new species (533.3 eV) matches well with typical adsorbed oxygen dimers on metals.[9] This clearly demonstrates that a part of the formal O^{2-} ions undergoes a dimerization of O_2^{2-} ions below the superconducting transition temperature.[10]

We have also followed the changes in the Cu(2p) spectra in this oxide as a function of temperature [Fig. 3(a)]. The peaks at ~933 and 953 eV are due to the spin-orbit doublet of the well-screened $3d^{10}$ states, whereas the feature at higher binding energies (~942 and 962 eV) are due to the poorly screened $3d^9$ states. On lowering the temperature to 80 K, we find clear evidence for an increase in the intensity of the $3d^{10}$ species compared to the $3d^9$ species. We consider this to be due to the formation of Cu^{1+} below the superconducting transition; Cu^{1+} should indeed be formed by the reduction of Cu^{2+} concomitantly with the dimerization of oxygen.

Further support for the reduction of Cu^{2+} to Cu^{1+} below T_c comes from the Cu (L_3VV) Auger spectra [Fig. 3(b)]. At 80 K we find a distinct feature at 915-eV kinetic energy which is weak in the spectra recorded at 300 K. Comparing the spectra with those of CuO and Cu_2O, we identify this feature as due to Cu^{1+} species.[10]

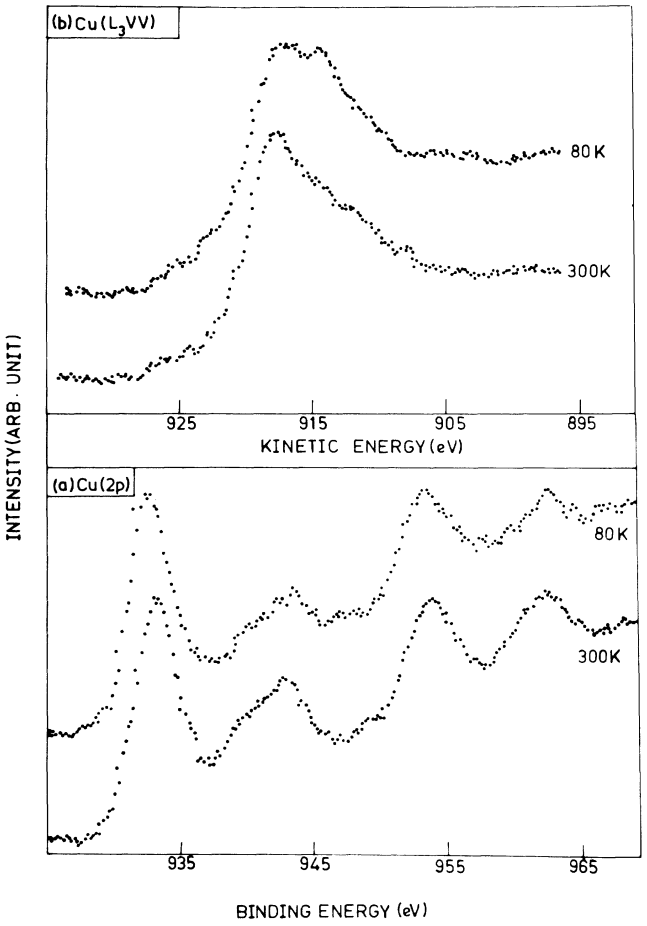

FIG. 3. (a) XPS of Cu(2p) region in $YBa_2Cu_3O_{7-\delta}$ at 300 and 80 K. (b) X-ray initiated Auger spectra of Cu (L_3VV) region in $YBa_2Cu_3O_{7-\delta}$ at 300 and 80 K.

In conclusion, the present study provides the first direct evidence for the dimerization of oxygen and the concomitant reduction of Cu^{2+} to Cu^{1+} in $YBa_2Cu_3O_{7-\delta}$ in the superconducting state. These findings as well as the observation of low density of states at E_F, lend support to the model proposed by Varma, Schmitt-Rink, and Abrahams[7] for high T_c of these oxide superconductors. It seems that holes in the oxygen 2p valence band give rise to resonating O–O bonds due to hole-hole coupling; this could indeed be involved in forming Cooper pairs. Preliminary studies of $La_{2-x}Sr_xCuO_4$ have also shown the presence of O_2^{2-}-like species which increase in intensity with the lowering of temperature.

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[10]Preliminary studies have shown that the O_2^{2-}-like species exist even at room temperature. The 533-eV peak due to this species in XPS increases progressively with decreasing temperature, just as the intensity above 8-eV binding energy in He II spectrum. The Cu (L_3VV) Auger signal due to Cu^{1+} also seems to increase with decreasing temperature. It is curious that we have no direct electron spectroscopic evidence for Cu^{3+} in the sample.