

Temperature-dependent change of Cu—O bond length in $\text{YBa}_2\text{Cu}_3\text{O}_7$

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X-ray photoelectron spectroscopy of the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ is performed, varying the temperature of the measurement (350, 230, and 180 K). The intensity of the O 1s peak corresponding to the Cu—O bond decreased with decreasing temperature. The intensity of the peak due to the electrons in the Cu 3d—O 2p antibonding orbitals with x^2-y^2 symmetry measured at 180 K is much smaller than that measured at 350 K. The top of the valence-band spectrum shifted -0.5 eV at 180 K relative to that at 350 K. A decrease of the O atoms in the crystal at lower temperature is observed in this experiment.

Bednorz and Müller¹ first reported high-temperature ($T_c \sim 30$ K) superconductivity in the La-Ba-Cu-O system and many other workers have investigated these materials and have recorded high superconducting transition temperatures.²⁻⁴ The Y-Ba-Cu-O system shows a higher T_c (~ 90 K) than the La-Ba-Cu-O system.^{5,6} At present it is of great interest to elucidate the origin of the high- T_c superconductivity.

In this paper we study the temperature-dependent character of the bond between Cu and O atoms dominated by the instability of the Cu—O bond in the basal plane of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ by using x-ray photoelectron spectroscopy as a first step toward understanding the high- T_c superconductivity of the Y-Ba-Cu-O system.

The samples were prepared from Y_2O_3 , BaCO_3 , and CuO powders. These powders were mixed and calcined at 1200 K for 5 h in an oxygen atmosphere. After that, the black powder obtained was milled, dried, granulated, and molded. The molded sample (13.5 mm \times 19.0 mm \times 4.0 mm) was heated at 1230 K for 3 h in oxygen. X-ray diffraction⁶ confirmed that the samples were well crystallized and over 95% single phase. Resistivity measurements were made by the four-point method over the temperature range 295–50 K. The magnetic susceptibility was measured by an ac inductance bridge. The onset and width of the transition depended on sample preparation methods, as reported by previous authors on the La-Ba-Cu-O systems.^{1,2}

The best samples had onset temperatures near 95 K. Photoelectron spectroscopy of the Y-Ba-Cu-O system was performed on the same sample used in the measurements of resistivity and magnetic susceptibility. X-ray diffraction⁶ and neutron diffraction data⁷ of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ sample showed orthorhombic structure. The structure can be described essentially as a layered structure of the central layer of a CuO_6 octahedron stretched along the c axis and the other layer which possesses a CuO_5 pyramid arrangement. It is obvious, as similarly predicted in other previous papers,^{8,9} that the electronic structure is dominated by the layered character of the crystal structure arising from the in-plane Cu 3d and O 2p

electron interactions forming d - p sigma bonding orbitals. The distance between the Cu and O atoms along the a axis was 1.942 Å, which is longer than that along the b axis (1.911 Å). The lattice parameters were $a = 3.883$, $b = 3.822$, and $c = 11.690$ Å. The interactions between the Cu and O atoms along the c axis are considered quite weak. It is easily seen that a wide band centered around 3 eV below the Fermi level is formed due to the strong interactions between the Cu and O atoms in plane, and that the Cu 3d electrons in nonbonding orbitals are strongly localized on the Cu atoms. A Fermi surface may nest in the [110] direction.

A VG Scientific ESCALAB-5 electron spectrometer was used to collect photoemission spectra with Mg $K\alpha$ radiation. The linewidth for the Ag 3d_{5/2} photopeak was 1.15 eV. The spectrometer was calibrated by utilizing the energy difference between Mg and Al $K\alpha$ radiation. The

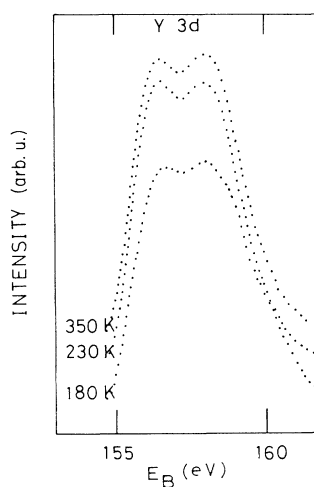


FIG. 1. The Y 3d electron spectra measured at 350, 230, and 180 K. The electron binding energy of the Y 3d_{5/2} and the splitting of the $\frac{5}{2}$ and $\frac{3}{2}$ are in good agreement with those of Y_2O_3 (Ref. 10).

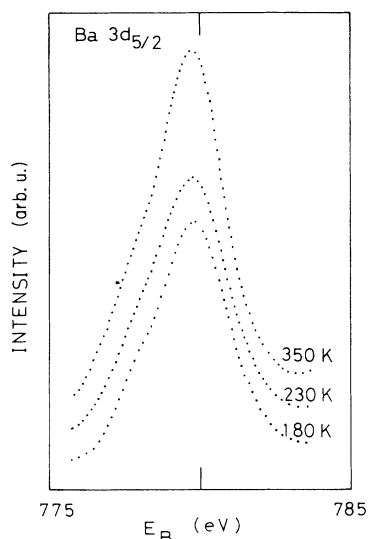


FIG. 2. The Ba $3d_{5/2}$ electron spectra measured at 350, 230, and 180 K. The main peak corresponds to that of BaO (Ref. 10) and the shoulder of the lower binding-energy side may be due to metallic Ba.

Pd $3d_{5/2}$, Ag $3d_{5/2}$, and Au $4f_{7/2}$ electron binding energies of the metal foils were 335.4, 368.3, and 84.0 eV, respectively. The probable electron energy uncertainty amounted to 0.1 eV. The normal operating vacuum pressure was less than 3×10^{-8} Pa. The electron binding energies were referred to the C $1s$ line of impurity carbon, which had a value of 284.6 eV. This value was consistent with a zero binding energy for the Fermi level.

The core-level spectra of Y, Ba, Cu, and O of the $YBa_2Cu_3O_7$ sample, measured at 350, 230, and 180 K, are shown in Figs. 1–4. The core-level electron binding energy of the Y atom was 156.5 eV, which is in good agreement with Y_2O_3 (Ref. 10) and that of the Ba atom was

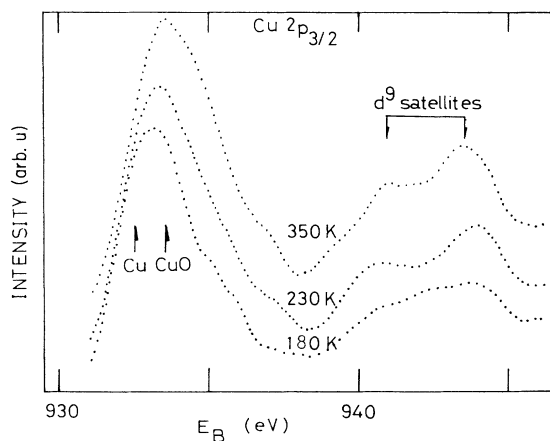


FIG. 3. The Cu $2p_{3/2}$ electron spectra measured at 350, 230, and 180 K. The chemical state of the Cu atom is considered to be CuO from the position of core level and the structure of the satellite. At 180 K the Cu metallic state increases and the peak position shifts to the lower binding-energy side.

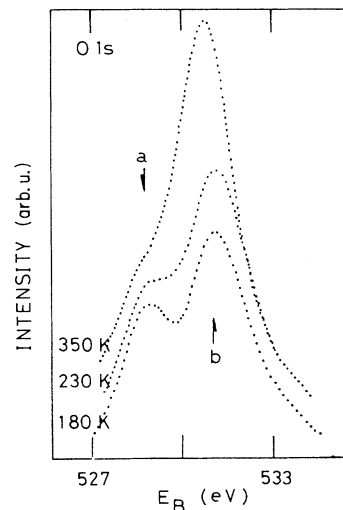


FIG. 4. The O $1s$ electron spectra measured at 350, 230, and 180 K. Peak *a* corresponds to the Ba—O and Y—O bonds. Peak *b* corresponds to the Cu—O bond. The intensity of peak *b* decreases with decreasing temperature.

779.7 eV, which is in good agreement with BaO.¹⁰ The lower binding-energy side shoulder of the Ba spectra may be due to metallic Ba.¹¹ The core-level electron binding energy of the Cu atom was 933.6 eV, which is in good agreement with CuO (Ref. 10), and the satellite structure of the spectra confirms that the systems are in a d^9 electron state such as the Cu(II) ion.¹² The O $1s$ electron binding energy of Y_2O_3 has not yet been reported; that of BaO is reported as 528.6 eV (Ref. 11) and that of CuO is reported as 530.3 eV.¹³ It is possible to partition the chemical bond of the O atom into three characters corresponding to Y_2O_3 , BaO, and CuO.

The core-level electron spectra of the Y and Ba atoms were invariant with respect to changes in the measurement temperature. The core-level electron spectra of the Cu atoms were different in detail. At 180 K the component of metallic Cu increased slightly. The O $1s$ spectra differed with the temperature. As shown in Table I, the number of O atoms decreased with decreasing measurement temperature. In particular, the intensity of the O $1s$ spectra of the Cu—O bond decreased with decreasing temperature, as shown in Table I. No change in the intensity of the O $1s$ spectra due to the other bond characters was observed with temperature variation. This result is consistent with those shown in Figs. 1 and 2. It is clear that the O atoms bonded to the Cu atoms decreased with decreasing temperature. The lattice instability in the

TABLE I. The atomic ratios of oxygen to other metals in the crystal and the intensity ratios of the oxygen peaks *b* to *a* in Fig. 4.

Temperature (K)	350	230	180
Atomic ratios [O/(Y+2Ba+3Cu)]	7.4	6.7	4.4
Intensity ratios (<i>b/a</i>)	1.9	1.7	1.3

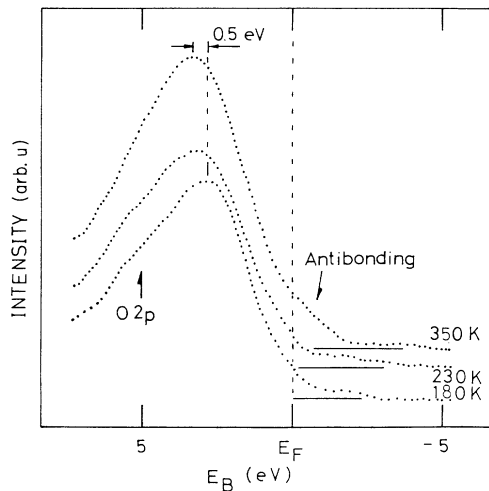


FIG. 5. The valence-band spectra measured at 350, 230, and 180 K. The intense peak around 3 eV is Cu $3d$ -O $2p$ σ bonding. The peak corresponding to Cu-O antibonding orbitals positioned 1 eV above the Fermi level decreases with decreasing temperature. The peak top of the valence band shifts to the lower binding-energy side with decreasing temperature.

basal plane of the Y-Ba-Cu-O systems is enhanced with lower temperature because the O atoms decrease with decreasing temperature.

The valence-band spectra are shown in Fig. 5. The intense peak positioned at ~ 3 eV is due to strong interactions between the Cu $3d$ electrons and the nearest-neighbor O $2p$ electrons with x^2-y^2 symmetry in the x - y plane, and it has a tendency to split with decreasing temperature into two peaks: Cu $3d$ and O $2p$. Below 230 K, the component of the O $2p$ orbital apparently appears at ~ 5 eV and decreases in intensity with decreasing temperature. The peak due to the Cu $3d$ orbital shifts to the lower binding-energy side. The enhancement of the deficiency of O atoms in the x - y plane at lower temperatures increases the intensity of the component of the Cu $3d$ -Cu $3d$ π bond. The intensity of the peak due to the electrons in the Cu-O antibonding orbitals decreases with decreasing temperature. Lower than 230 K it is obvious that the peak intensity of the Cu-O antibonding orbitals is much smaller than that measured at 350 K. The electron binding energy of the Cu $3d$ level measured at 180 K shifts -0.5 eV relative to that measured at 350 K.

The total pressure and partial pressures of the components of the residual gas in UHV were measured by an AQA 360 residual gas analyzer of Anelva Corporation, and are shown in Fig. 6 as a function of the cooling time of the sample with liquid nitrogen through the ESCALAB-5 cooling pipe leading to the rotary pump.

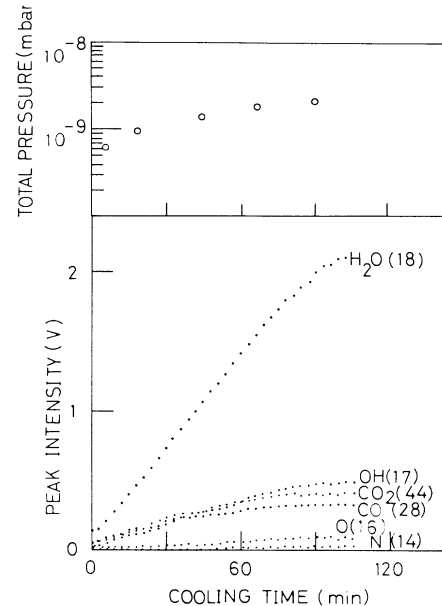


FIG. 6. Total pressure of the residual gas and partial pressures of the components in UHV of ESCALAB-5 vs the cooling time of the sample by liquid nitrogen. The increase of total pressure and those of the partial pressures of H_2O , OH, CO, and CO_2 are parallel. Of course no change of the total pressure in UHV was observed for cooling of the sample holder with no samples.

The total pressure increased with increasing cooling time. The partial pressure of H_2O (mass number 18) increased drastically, and those of OH (17), CO (28), and CO_2 (44) increased slightly. The intensity of the peak of mass number 14 due to N was very small. The peak of mass number 28 is dominated by CO. The increase of total pressure and partial pressures is consistent with the results of the photoemission experiment, i.e., of decreasing oxygen atoms at lower temperature.

It is possible that the decrease of the electron population in the antibonding orbitals make the wave functions localize on the Cu and O atoms. The enhancement of the oxygen deficiency in the x - y plane of the crystals makes the effective interactions at the Fermi level more attractive at lower temperature. The enhancement of the oxygen deficiency at lower temperature accompanies the increase of the lattice instability of the crystals and may correlate with the commensurate-incommensurate phase transition of the $YBa_2Cu_3O_7$ crystals. Charge-density waves in the two-dimensional systems such as Y-Ba-Cu-O may give rise to high- T_c superconductivity similar to La_2CuO_4 crystals.^{9,14}

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