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Temperature-dependent change of Cu–O bond in La_2CuO_4 and $YBa_2Cu_3O_7$

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Valence-band spectra of La_2CuO_4 and $YBa_2Cu_3O_7$ were obtained by using X-ray photoemission varying the temperature of the measurement (35, 260, 300, and 500° C). In La_2CuO_4 the broad band centred around 4 eV splits into two peaks at 260° C. At both 35 and 500° C the spectra show almost similar shape. In $YBa_2Cu_3O_7$ the broad peak centred around 4 eV splits into two peaks at 500° C. Below 300° C the spectra show almost similar shape. These splittings of the valence-band spectra may be due to the rearrangement of the crystal structure accompanying the phase transition from the orthorhombic to tetragonal symmetry.

1. Introduction

Since the discoveries of high temperature superconductivity by Bednorz and Müller (30 K) in a La–Ba–Cu–O system [1] and Chu and colleagues (90 K) in a Y–Ba–Cu–O system [2], much effort has been made to investigate the electronic structure of the high-T_c superconductors.

The crystal structure of the superconducting phase of $(La_xBa_{1-x})_2CuO_4$ is reported to be the tetragonal K_2NiF_4 type [3]. This structure is described in terms of alternating layers of perovskite type ($KNiF_3$) and rock salt type (KF) units along the c axis. The superconducting phase in Y–Ba–Cu–O system, identified as $YBa_2Cu_3O_{6.9}$ [4], is reported to be orthorhombic [5–7]. The structure can be described essentially as a layered structure. The Cu(I) atoms on the $z = 0$ plane are believed to form fence-like chains of $[Cu(I)O_4]$ planes parallel to the [0 0 1] direction, and these chains extend linearly along the [1 0 0] direction. The central layer of a $Cu(I)O_4$ fence-like chain separates the upper and under layers which possess a $Cu(II)O_4$ square planar arrangement. In both systems of the high-T_c superconductor 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 σ bonding orbitals.

The nonsuperconducting end-member compound La_2CuO_4 is a typical semiconductor and is a prototype of two-dimensional superconducting material. Grant and co-workers [8] have reported trace superconducting behaviour in La_2CuO_4. Superconduction may occur only in the planes containing the $LaCuO_3$ perovskite layers. In La_2CuO_4 the orthorhombic structure ($a = 0.5363$, $b = 0.5409$, and $c = 1.317$ nm), which is stable at room temperature and the copper have two long Cu–O distances (0.240 nm) and four short distances (0.190 nm), becomes tetragonal at 260° C without any significant change in Cu–O distances [9]. Nakamura and co-workers [10] have reported the orthorhombic to tetragonal phase transition around 500° C of $Y_{1.2}Ba_{1.8}Cu_3O_{6.7}$ in an argon atmosphere. The electronic structure in both La_2CuO_4 and $YBa_2Cu_3O_7$ should change around the transition temperature with the rearrangement of the crystal structure.

In this report we show the change of Cu–O bond in La_2CuO_4 and $YBa_2Cu_3O_7$ versus temperature by using X-ray photoemission.

2. Experimental procedures

The La_2CuO_4 samples used in this experiment were non-superconductors and prepared by the operations described by Longo and Laccah [9]. Powder X-ray diffraction on the samples indicated with the orthorhombically distorted K_2NiF_4 structure is as shown in Fig. 1. The atomic ratio of La to Cu was 2.3, which was determined by inductively coupled plasma optical emission spectrometry (ICPOES). The ratio of O to Cu was 4.4, which was determined by Horiba EMGA-2800 oxygen analyzer using graphite crucible RF combustion and CO infrared absorption spectrometry [11]. The $YBa_2Cu_3O_7$ samples were prepared from Y_2O_3, $BaCO_3$, and CuO powders. These powders were mixed and calcined at 900° C for 5 h in air. After that, the black powder obtained was milled, dried, granulated, and moulded. The moulded sample was heated at 950° C for 10 h in air. X-ray diffraction showed that the samples had orthorhombic structure as shown in Fig. 2a. The $Y_1Ba_2Cu_3O_{6.9}$ composition was determined by using the ICPOES and EMGA-2800 oxygen analyzer [12].

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 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 $1s$

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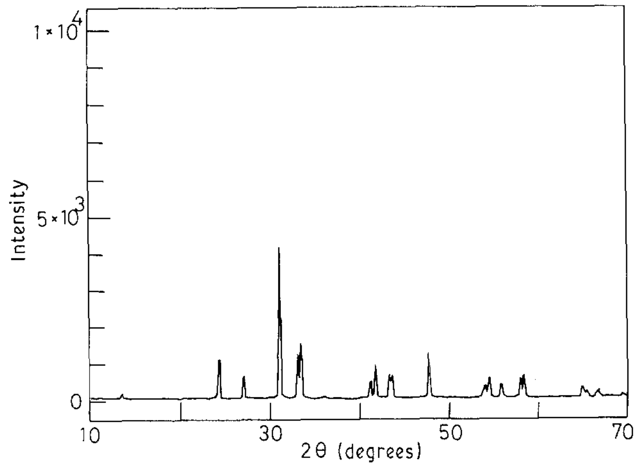
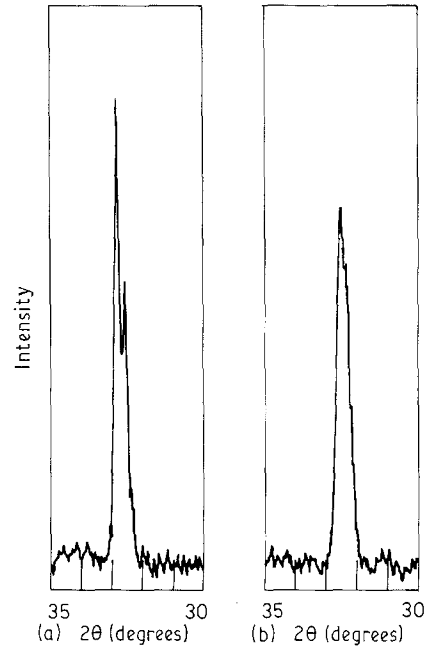


Figure 1 X-ray diffraction pattern of the La_2CuO_4 sample before heating in UHV.

line of carbon atom, which had a value of 284.6 eV. This value was consistent with a zero binding energy for the Fermi level. The sample was heated with the heater of the ESCALAB-5. A digital thermometer (YEW 2572) with an alumel-chromel thermocouple was used to measure the temperature.

3. Results and discussion

Recently many calculations of the band structure have been performed on the body-centered-tetragonal (bct) phase (space group D_{4h}^{17}) on La_2CuO_4 [13–16] and on the $YBa_2Cu_3O_7$ [16]. It is obvious that the electronic structure is dominated by the layered character of the crystal. The distance between the Cu and O atoms along the c axis was 0.240 nm which is longer than that in the xy plane (0.190 nm) in La_2CuO_4. In $YBa_2Cu_3O_7$ the Cu(I) atoms have two short Cu(I)–O bonds (0.1808 nm) and two long Cu–O bonds (0.1932 nm), in $Cu(I)O_4$ fence-like plane and in upper and under two-dimensional square planes the Cu(II) atoms have four short Cu(II)–O bonds (0.1944 nm). And the distance between Cu(II) atoms and O atoms along the c axis of $[Cu(I)O_4]$ fence-like chain is 0.2434 nm [7].



(a) 2θ (degrees) (b) 2θ (degrees)

Figure 2 X-ray diffraction pattern of the $YBa_2Cu_3O_7$ sample, (a) before and (b) after heating in UHV.

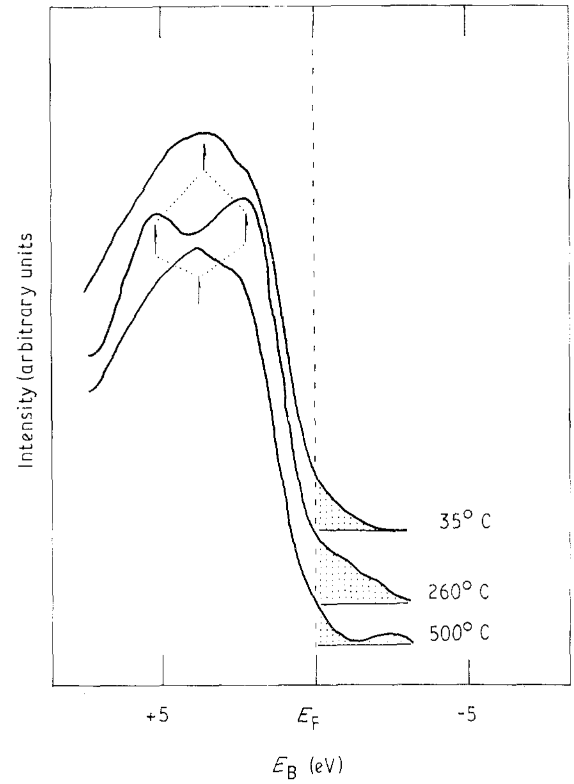


Figure 3 The valence-band spectra of La_2CuO_4 sample measured at 35, 260, and 500° C.

The valence-band spectra measured at 35, 260 and 500° C of the La_2CuO_4 sample are shown in Fig. 3. In Fig. 4 the valence-band spectra of the $YBa_2Cu_3O_7$ sample measured at 35, 300 and 500° C are shown.

In Fig. 3 almost similar spectra were obtained at 35 and 500° C. These spectra may reflect the ordered Cu–O bond in both orthorhombic and tetragonal phases of La_2CuO_4. The peak centred around 4 eV is formed by the electrons in the Cu $3d$(xy, yz, xz) and (z^2) orbitals in the stretched CuO_6 octahedra. The crystal field due to the elongated O_6 octahedra removes the orbital degeneracy of the Cu^{2+} d^9 configuration and leaves the Cu $3d(x^2-y^2)$ orbital as the only partially occupied atomic orbital. At 260° C (orthorhombic to tetragonal phase transition temperature) the valence–band spectrum split into two peaks positioned around 2 and 5 eV. The low binding energy peak (2 eV) is formed by the electrons in the Cu $3d(x^2-y^2)$ orbitals. The high binding energy peak (5 eV) is formed by the electrons in the O $2p$ orbitals. The Cu $3d(z^2)$ orbitals are filled in La_2CuO_4. Since the Cu–O–Cu interactions are much stronger for the Cu $3d(x^2-y^2)$ orbitals than the Cu $3d(z^2)$ orbitals, the Cu $3d(x^2-y^2)$ orbitals are half filled. Pickett and Krakauer [14] have pointed out that the Cu t_{2g} contribution to the density of states at the Fermi level is zero and the Cu e_g molecular orbital crosses the Fermi level in $LaCuO_3$ perovskite. The single hole per Cu^{2+} ion occupies an orbital that is antibonding not only with respect to the anions, but also respect to the copper ions [17]. Deformation of the Cu^{2+} ion octahedral site raises the top of the Cu $3d(x^2-y^2)$ band above the

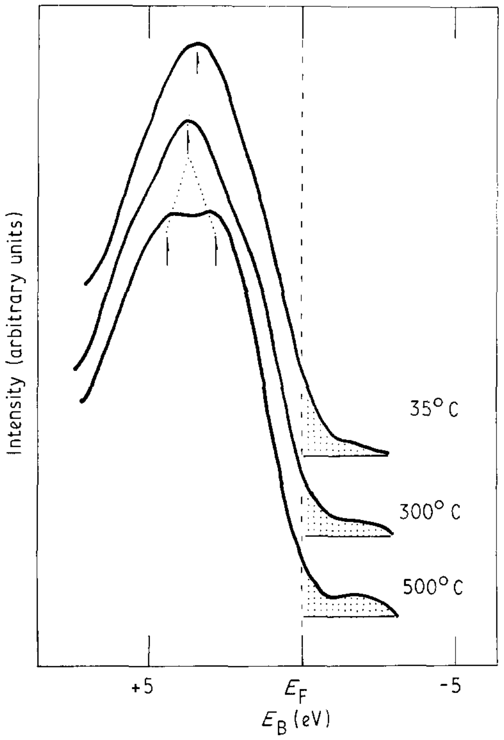


Figure 4 The valence-band spectra of $YBa_2Cu_3O_7$ sample measured at 35, 300, and 500° C.

$d(z^2)$ level, since the Cu $3d(x^2-y^2)$ orbitals are antibonding with respect to the O $2p$ orbitals. The spectral intensity of the Cu $3d(x^2-y^2)$–O $2p(x, y)$ antibonding orbitals crossing over the Fermi level measured at 260° C is larger than that at both 35 and 500° C. This change of the valence-band spectra observed at 260° C may reflect the electron delocalization due to rearrangement of the Cu–O bond ordering from the orthorhombic phase to tetragonal phase.

In Fig. 4 the peak centred around 4 eV due to the Cu $3d(xy, yx, xz)$ and (z^2) orbitals was obtained at both 35 and 300° C. The spectra measured at 35 and 300° C correspond to the orthorhombic structure. The spectrum obtained at 500° C split two peaks as is similarly observed in La_2CuO_4 at 260° C. The lower binding energy side shoulder is formed by the electrons in the Cu $3d(x^2-y^2)$ orbitals and the higher binding energy side shoulder is formed by the electrons in the O $2p$ orbitals. The peak intensity of the electrons in antibonding orbitals crossing over the Fermi level measured at 500° C is much larger than that below 300° C. This change of the valence-band spectra may correspond to the electron delocalization stimulated by the rearrangement of the Cu–O bond at the orthorhombic to tetragonal phase transition temperature in UHV because the orthorhombic to tetragonal phase transition occurs at around 500° C in argon atmosphere [10]. As shown in Fig. 2b, the X-ray diffraction pattern indicated the transition from orthorhombic to tetragonal phase in bulk ceramics. The increase of the electron population in the antibonding orbitals crossing over the Fermi level makes the wave functions delocalize on the Cu and O atoms. The increase of the electron occupation near the Fermi level makes the Cu–O interaction less attractive.

Finally, temperature-dependent Cu–O bond changes in both La_2CuO_4 and $YBa_2Cu_3O_7$ samples at the orthorhombic to tetragonal phase transition temperature were observed. The main peak centred around 4 eV split into two peaks corresponding to the electrons in the Cu $3d(x^2-y^2)$ orbitals and O $2p$ orbitals. The peak intensity of the antibonding orbitals increased at the phase transition temperature. These changes cause the wavefunctions to delocalize on the system and the Cu–O interaction to be less attractive.

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