Photoemission on the High $T_c$ Superconductors Y–Ba–Cu–O

P. Steiner, V. Kinsinger, I. Sander, B. Siegwart, and S. Hüfner
Fachbereich Physik, Universität des Saarlandes, Saarbrücken, Federal Republic of Germany

C. Politis
Institut für Nukleare Festkörperphysik, Kernforschungszentrum Karlsruhe, Karlsruhe, Federal Republic of Germany

Received April 16, 1987

XPS and UPS photoemission experiments on the high $T_c$ superconductors ($T_c \approx 90$ K) with nominal composition YBa$_2$Cu$_3$O$_{9-y}$ ($y \approx 2$) show the following:

a) The density of electronic states at the Fermi energy is very small, much smaller than in pure Cu.

b) The Cu 2p spectra show only a Cu$^{2+}$ contribution.

c) The Ba core levels show a structure with two components of nearly equal magnitude, which leads to the suggestion that these compounds have large O$^{2-}$ vacancies coordinated to Ba$^{2+}$ sites.

d) Annealing at 400 °C under UHV conditions leads possibly to a partial reduction of Cu$^{2+}$ to lower Cu valence states and to a small increase of the O$^{2-}$ vacancy component of the Ba$^{2+}$ line.

The initial work of Bednorz and Müller [1, 2] on the superconductivity in the La–Ba–Cu–O system with $T_c$ values around 30 K started investigations in many laboratories [3–8] to synthesize new superconducting compounds based on the La$_2$CuO$_4$ system with transition temperatures between 30 K and 50 K. Recently superconductivity with very high $T_c$'s above 90 K have been realized in the Y–Ba–Cu–O system [9–11]. The first samples of these compounds were multiphased systems of nominal composition Y$_{1.2}$Ba$_{0.8}$CuO$_4$ [9], but now single phased compounds of nominal composition YBa$_2$Cu$_3$O$_{9-y}$ [11] have been synthesized with a superconducting transition around 100 K and a width of the transition of only a few K.

The physical mechanism leading to these high transition temperatures is completely unclear. But it becomes more and more evident that the electronic properties of these compounds are not very different from similar oxide systems and that the electronic density of states at the Fermi energy is small [12–15], so that unusual phononic properties [16–19] must be responsible for the superconductivity in this class of compounds.

To get more insight into the electronic and chemical properties of the Y–Ba–Cu–O system we have performed XPS and UPS photoemission experiments. While first experiments on Y$_{1.2}$Ba$_{0.8}$CuO$_4$ (nominal composition) samples gave badly resolved XPS spectra [15] due to inhomogeneities in these multiphased samples, experiments on nearly single phased YBa$_2$Cu$_3$O$_{9-y}$ ($y \approx 2$) showed very well resolved XPS core level spectra. The samples were prepared as described in Ref. 10. The experiments were performed in a VG ESCALAB MKII, equipped with an Al $-K_x$/Mg $-K_x$ twin anode, monochromatized Al $-K_x$ radiation source and a He discharge lamp for He $-I$ (21.2 eV) and He $-II$ (40.8 eV) radiation. The samples were mechanically clamped to the sample holder and cleaned in situ by scraping with a diamond file. The only contamination which could be detected by core level spectroscopy was a few percent carbon in the
form of CO or CO$_2$, probably due to adsorption of these gases at inner surfaces of these not completely dense samples. From core level intensities, and with a La$_2$CuO$_4$ sample as a standard the Cu/O ratio is determined as 0.42 in agreement with the nominal composition YBa$_2$Cu$_3$O$_7$.

Figure 1 compares He–I (21.2 eV), He–II (40.8 eV) and Al-K$_\alpha$ (1486.7 eV) spectra of a YBa$_2$Cu$_3$O$_7$ sample. The experimental energy resolution for the He spectra was set to about 0.2 eV and to about 0.5 eV (monochromatized XPS) for the XPS spectrum. The position of the Fermi energy was carefully located by Cu-metal spectra from Cu evaporated in situ onto the sample. As can be seen from the spectra the spectral intensity close to the Fermi level is very small. The spectral features around 4 eV are dominated by the Cu–3d and O–2p derived levels, where the O–2p derived feature near 4.5 eV increases slightly as compared to the Cu–3d derived structure near 3.5 eV when going from He–II to He–I radiation, while the structure is completely smeared out in the XPS spectrum, a behaviour which generally is expected from cross section arguments. Near 9 eV in the He–II spectrum a peak from the carbon contamination shows up. The general behaviour of the valence band structures is not very different from the ones observed in the La–Cu–O system [12–15] and agrees qualitatively with the density of states calculations, recently presented by Mattheis [17]. But the density of states at $E_F$ is much smaller than expected for metallic conductivities. This is demonstrated in Fig. 2 where we compare He–I spectra of Cu, La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_7$. The intensity in the spectra has been normalized to the peak amplitude of the Cu–3d derived structure (Fig. 2a).

The region around the Fermi energy $E_F$ is shown in Fig. 2b in an enlarged scale. Since it is well known [20] that the He–I resonance line at 21.2 eV has weak satellites at 23.1 eV (intensity about 2%) and 23.7 eV (intensity about 0.5%) we have to consider the fact that these satellites produce structures near the Fermi edge via satellite excitation from the intense (Cu–3d; O–2p) band. Figure 2c shows the Fermi edge region corrected for these satellites. This gives a well defined step at the Fermi edge for Cu and leaves nearly no intensity at $E_F$ for the La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_7$ samples. The extrapolated upper edge of the (Cu–3d; O–2p) valence band is 1.03 eV for La$_2$CuO$_4$ and 0.48 eV for YBa$_2$Cu$_3$O$_7$. The intensity at $E_F$ in these samples per Cu atom is at least an order of magnitude smaller than in pure Cu. This means that either the density of states at $E_F$ is very small, much smaller than e.g. given in the DOS calculations in Ref. 17, or that the photoexcitation cross section for these electrons at 21.2 eV is very small as compared to the O–2p or Cu–3d electrons, or both.

XPS core level spectra measured in normal emission for the elements in YBa$_2$Cu$_3$O$_7$ are shown in Fig. 3, measured with high resolution of 0.5 eV. The Y–3d spin-orbit doublet is well resolved. The Cu–2p spectrum is the one as expected for Cu$^{2+}$ oxides [21] with the typical Cu$^{2+}$ satellite structure. It is sometimes assumed that a mixed Cu$^{2+}$/Cu$^{3+}$ valence state is responsible for the unusual properties of these compounds [1, 2]. The position and width of the main Cu–2p 3/2 line is exactly the same as the one observed in La$_2$CuO$_4$, as shown in Fig. 4, while the satellite intensity is 10% smaller. If we assume that in La$_2$CuO$_4$ the Cu ion is in a pure Cu$^{2+}$ state, then there is no indication of a Cu$^{3+}$ component in the spectra. The O–1s and Ba–3d 5/2 spectra in Fig. 3 clearly consists of two contributions a) and b). While the satellite b) in the O–1s spectrum increases by a factor of two when going from normal emission to a glancing take-off angle of 75° with respect to the sample normal, we observe no change in the O–1s spectra a) when going from normal to grazing emission.