

## VALENCE BAND STUDIES OF YBaCuO THIN FILMS

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We studied the valence bands of  $Y_1Ba_2Cu_3O_7$  by means of X-ray Photoelectron Spectroscopy, Bremsstrahlung Isochromat Spectroscopy and optical reflectivity. We show, that the room temperature reflectivity has metallic characteristics. On the other hand in both the occupied and unoccupied states as measured by XPS and BIS the density of states close to the Fermi level is very low, which is characteristic of a semiconductor.

### 1. SAMPLE PREPARATION

The experiments described in this paper were performed on thin films of YBaCuO, which were prepared by means of three metal co-deposition and simultaneous oxidation. The substrates were single crystal  $Al_2O_3$ . The samples were black and shiny and the composition as determined from electron microprobe analysis was within 3% of the nominal 1:2:3:7 composition.

The XPS and BIS experiments were performed in a combined XPS/BIS spectrometer. After insertion in the vacuum chamber the samples were cleaned by means of Ar ion etching and annealing under 0.01 (Torr) of oxygen. The effect on contamination, composition and core level line shape were followed with XPS. A detailed discussion of the Cu 2p and O 1s core level spectra as well as the Cu LMM and O KLL Auger spectra has been given elsewhere (1).

### 2. EXPERIMENTAL

The XPS spectrum displayed in Figure 1 was taken with Al K $\alpha$  radiation. The structure at about 14-15 (eV) binding energy is due to the Ba 5p states. The shoulder at about 10 (eV) binding energy is usually attributed to a "satellite" which in this case would have predominantly Cu  $d^8$  final state character. The broad structure between 0 (eV) and about 7 (eV) is then assigned to predominantly O 2p states. As observed in numerous other investigations the density of states observed close to the Fermi level is very small and is more typical of a semiconducting rather than a metallic system (2). From bandstructure calculations (3) one would expect a sizable density of states at  $E_F$ . This discrepancy is due to the strong electron-electron correlations. Usually, if strong correlations are present, bandstructure calculations based on the local density approach do not provide the correct single hole or single electron excitation energies.

In Figure 1 we also display the BIS spectrum of the unoccupied conduction bands using a 1486.6 (eV) X-ray monochromator for bremsstrahlung detection. We interpret the peak at 2.5 (eV) as the Cu  $d^{10}$  final state. The wide band starting at about 8 (eV) then consists of mixed O 3s, Cu 4s, Ba 5d and Y 4d character, while the narrow peak at 15 (eV) is formed by the unoccupied Ba 4f resonance. The total resolution of the BIS setup is about 0.7 (eV), so that the tail extending to the Fermi energy is probably due to instrumental

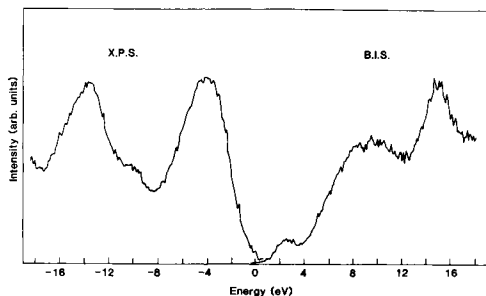


FIGURE 1  
XPS and BIS valence band spectra.

broadening.

We collected optical reflectance spectra in the energy range between 0.1 and 6 (eV) at room temperature. The dielectric function was determined from the spectra by means of Kramers-Kronig analysis. The real part of the dielectric function crosses zero at about 0.8 (eV) and diverges for longer wavelengths. Therefore we interpret the corresponding longitudinal mode as the plasma mode. Assuming the free electron value for the charge carrier mass, and using a Drude analysis of the data we obtain a carrier density of  $7.3 \times 10^{20}$  ( $\text{cm}^{-3}$ ). This corresponds to 0.12 elementary charges per unit cell.

In Figure 2 we display the optical conductivity, which was calculated from the imaginary part of the dielectric function. There are broad structures in the conductivity plot near 1.3 (eV) and 2.3 (eV), followed by a minimum at 3.2 (eV) and a wide absorption band at higher energies. The peak at 0.4 (eV) coincides with the peak observed by Kamaras et al. (4). To point out where our combined BIS and XPS results put the onset of interband transitions, we also plot the convolution of the spectra of Figure 1, which corresponds to the experimentally determined joint density of states, apart from optical matrix elements and selection rules. We see that the main increase starts around 3 (eV) so that the structures at 1.3 and 2.3 (eV) cannot be due to straightforward interband transitions. We speculate, that these structures are pulled out of the continuum of interband transitions by strong electron-hole interactions.

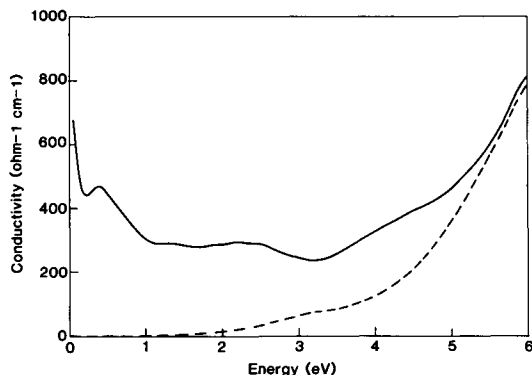


FIGURE 2

Conductivity function (solid curve) and convolution of XPS and BIS (dashed curve).

### 3. CONCLUSIONS

The high value of the electron electron repulsion energy (1) as well as the observation of a gap in the XPS and BIS spectra indicate, that the valence band structure of YBaCuO is dominated by strong electronic correlations. If no oxygen 2p bands were present this would mean, that the material becomes a Mott-Hubbard insulator with a correlation gap of 5 to 7 (eV). The oxygen 2p bands are located just below the Fermi energy and inside the Cu d-d gap, which implicates that the gap in  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$  is of charge-transfer rather than Mott-Hubbard type. This corresponds to region B of the Zaanen Sawatzky Allen classification scheme of transition metal compounds (5). Consequently the holes introduced upon addition of oxygen will be of primarily O 2p character. From our analysis of the optical data we find metallic behaviour at low frequencies. The real part of the dielectric function crosses zero at 0.8 (eV), which we interpret as the plasmon frequency. At lower frequencies the dielectric constant shows divergent behaviour typical for metallic systems. There are several broad structures in the conductivity plot between 1 and 3 (eV) which we interpret as transitions of excitonic origin.

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