Photoemission Spectroscopy of YBa$_2$Cu$_3$O$_{6+x}$

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High-resolution angle-integrated photoemission measurements were made on a sample of the compound Y$_1$Ba$_2$Cu$_3$O$_{6+x}$, for which it was shown that the onset of superconductivity was as high as 93 K. The density of states associated with the Cu 3d levels appears in an intense band about 4 eV wide beginning about 1.5 eV below the Fermi level. A small wing of this band extends up to the Fermi level, where the density of states is relatively low. These results are in good agreement with the projected density of states of Cu as obtained in recent calculations.

Since the announcement by Chu and co-workers$^1$ that superconductivity sets in at 98 K in the Y–Ba–Cu–O system, a very large amount of work has been done to identify the dominant phase and determine the essential properties of these new materials. For example, it has been learned that a composition close to YBa$_2$Cu$_3$O$_{6+x}$ with $x = 0.9$ results in the high $T_c$, and there are ordered O vacancies. The structure is basically one containing layers of Cu and O atoms, interleaved with layers containing only Y or Ba. Band calculations on this compound$^{2,3}$ as well as related materials$^4$ indicate a manifold of levels centered about 3 eV below the Fermi level $E_F$ consisting primarily of O 2p and Cu 3d states. So far there has been no direct experimental verification of this electronic structure. Here we use the technique of angle-integrated photoemission to provide an experimental density of states relative to $E_F$ as well as the binding energies of the various core levels in the material.
In the present experiment we measure a photoelectron energy distribution curve $N(E, h\nu)$, a function of both electron kinetic energy $E$ and photon energy $h\nu$. It is well known\(^5\) that $N(E, h\nu)$ depends upon both the initial density of states $\rho(E)$ and the photoionization cross section $\sigma(h\nu)$ for transitions between the initial bound-state wave function and final continuum wave function. For a valence band that is a mixture of $p$ and $d$ wave function, as a first approximation one can write

$$\begin{align*}
N(E, h\nu) &= \rho_p(E)\sigma_p(h\nu) + \rho_d(E)\sigma_d(h\nu) 
\end{align*}$$

The calculated atomic photoionization cross sections $\sigma_{p,d}$ are at least a guide to the behavior of the matrix elements for the core levels of various symmetry and for the more or less localized $d$ levels in the valence band. By using an intense beam of photons from a synchrotron radiation source, tunable over a wide energy range, it is possible to enhance one specific cross section or the other. In the present work the photon energy $h\nu$ was set close to 180 eV in order to make the Cu 3d cross section about ten times the O 2p photoionization cross section.\(^6\)

Samples were made by mixing and grinding BaCO$_3$, Y$_2$O$_3$, and CuO powders (all 99.999% pure) and reacting them in air at 950°C for 24 h with two intermediate grindings. The resulting material was ground and pressed into pellets with a pressure of 500 MPa applied for 5 min. The pellets were then removed from the press and treated in a stream of pure oxygen for 16 h at 900°C and for 16 h at 700°C. X-ray powder diffraction at this point revealed a single-phase sample of the expected structure.\(^7\) The magnetic transition, as measured by a superconducting quantum interference device-based (SQUID) magnetometer, had an onset temperature of 92 K with a midpoint around 60 K. Regrinding the pellets, pressing them again in the same manner, and annealing them in a stream of oxygen for 20 h at 700°C sharpened the magnetic transition considerably, giving the same onset temperature, but a higher midpoint: 82 K, as shown in Fig. 1. X-ray powder diffraction of this sample, which was used in the photoemission experiment, showed no change from the single-phase sample with the broader transition.

Angle-integrated photoemission experiments using synchrotron radiation were carried out in a manner previously reported for a manganese-doped Chevrel superconducting compound.\(^8\) A hemispherical electron energy analyzer was used for selected photon energies in the range 50-1500 eV from an extended range grasshopper monochromator\(^9\) on the 1-GeV electron storage ring at the Synchrotron Radiation Center, Stoughton, Wisconsin.

The pressed and sintered sample of YBaCuO was mounted against indium foil on a precision sample manipulator, which could be operated at temperatures down to about 80 K. The initial runs were made after